

January 30, 2019

Dear James Roberts,

We have now completed and uploaded responses to the referee comments on our manuscript, “pH-Dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces,” submitted to *Atmospheric Chemistry and Physics*. The referees gave very useful comments, and we feel we have faithfully and completely addressed all the reviewers’ concerns. We believe this process has produced a much-improved manuscript, and hope you find this revised paper is now in publishable form.

Sincerely,

John W. Halfacre

Response to Anonymous Referee #1

We would like to thank Anonymous Referee #1 for his/her careful reading of this manuscript and constructive suggestions. We have addressed all of his/her comments in the revised manuscript, and describe in detail changes made below in the order in which they were raised by the reviewer. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise. For clarity, the text of the reviewer's comments is in **black**, while the authors' responses are in blue.

The manuscript by Halfacre et al. describes a number of laboratory experiments conducted to better elucidate the nature of halogen activation from halide-containing ices. This is an important topic in polar boundary layer chemistry, and only a couple of lab studies have been performed on this system before. So there is inherent merit to the work in that regard.

The halogen release is driven either by exposure to ozone or by illumination when an OH radical precursor, such as nitrite or hydrogen peroxide, is incorporated into the frozen solution. The experiments are performed using a flow tube that is coupled to a chemical ionization mass spectrometer operated with an iodide reagent ion. The solutions also contain a buffer to maintain the acidity of the solution, given that protons are required for some of these activation processes. I have a few questions concerning the experimental approach (see below) but my major comments are related to the presentation of the experimental results, although I am in general agreement with their interpretations. Some of the results themselves are new and interesting (e.g. I₂ release in the dark) but others have been showed before, albeit with different approaches (e.g. Br₂ release with light).

I'll start by saying that I found this paper very challenging to read, especially the Results and Discussion sections which were excessively wordy. The Introduction and Conclusions are fine. Given that there are only a few figures of data, I believe that the experimental results and their discussion could be much more succinctly described, perhaps cut in length by a factor of two. As opposed to describing every observation, could the major findings be emphasized? Indeed, I recommend that the authors rewrite the paper so that the results and associated discussion are united, i.e. the results are discussed as they are presented. I found myself moving back and forth many times between the two sections as I was reading the paper.

Thank you for your comments and suggestions. We have been diligent in working to improve the readability of the manuscript. The Results and Discussion sections have been combined into Section 3, discussing results as presented, which we believe improved readability, as you suggested. An effort was made to make the new section more concise.

The Abstract, too, could be improved. For example, the authors should explain what they mean when they state that photochemical production of Br₂ was observed (line 33). What were the conditions that led to Br₂ production?

We have amended this sentence to clarify that photochemical production of Br₂ at low pH requires an OH precursor (lines 32-33).

Another example is that the mechanism of the heterogeneous recycling should be mentioned (line 35).

We have reworded this sentence to clarify that the gas phase HOX compounds would diffuse into our frozen sample solution to oxidize X⁻ (line 36)

Finally, the last sentence should point out that these mechanisms, even if slow, may be important as the initiation of halogen release to the atmosphere, even if it is found they do not ultimately constitute the major source.

We have included this statement at the end of our abstract (lines ~ 40-43), as suggested.

Another weakness of the paper is the attempt to connect the laboratory results to those measured in the field. There are so many factors that come into play in this chemistry, I don't think we can plan to quantitatively relate the lab and the field in the manner attempted. For example, is the spatial distribution of the salts, protons, and OH precursors the same in the field snow samples as those in the lab? I believe the answer is no, given the totally different manner by which the ice samples are prepared. For example, how might the buffer materials (such as acetate) interact with OH in the ice? Is the surface segregation of these species the same? My advice would be to give up on the goal of making that comparison, except in the most qualitative manner. My advice would be to give up on the goal of making that comparison, except in the most qualitative manner.

We have reevaluated our discussion points as a result of this comment and have removed, most notably, the calculation of relative production rates for the field based on our calculated relative reactivities. While we feel the calculation of relative reactivities represents an important empirical result, it is less defensible to apply them quantitatively to field observations derived from samples very different from ours, as the reviewer suggests.

Interactions between buffers and OH are discussed in more detail below under the more specific question from the reviewer. We have also incorporated discussion to this end in the Supplemental Information, lines 3-28.

The reviewer is also correct in implying vast differences in the spatial distribution of ions between our lab samples and field samples. We acknowledge and discuss this point in the paragraph that spans lines 386-407 in the revised manuscript.

That said, I do believe that the relative rate approach for interpreting the kinetics of oxidation of different halides has merit. There could be more done interpreting these reactivity ratios in terms of the (much better) known bulk aqueous reaction rate constants.

A comparison of our calculated relative reactivities with the bulk aqueous OH-halide rate constants, along with a discussion of the implications of the differences, has been included and begins on line 372.

Experimental questions-

Will the acetic acid/acetate buffer be affected by volatilization of acetic acid from the ice?

pH measurements were recorded before and after each experiment, but no statistically significant difference was observed. We have now clarified that this suggests no significant loss of the buffering capacity over the course of the experiment on lines 146-148.

I found line 128 confusing – i.e. was no iodide observed by IC? If so, what LOD was prevalent for the IC method?

Iodide was not observed above the observed limit of detection by IC. We have clarified this point and added the limit of detection for the method used (90 nM), line 327.

For the bisulfate buffer, will OH react with bisulfate to form the sulfate radical anion, rather than react with the halide ions?

This reaction pathway will indeed occur, potentially followed by reaction with the halides.



However, the OH reactions rates with the halides are >10,000 faster ($k_{\text{Cl}^-} = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{\text{Br}^-} = k_{\text{I}^-} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$). We calculate that the sulfate radical would contribute less than 0.1% to halide oxidation, compared that from OH-halide oxidation. Because this is only believed to influence the results to a minor degree, we have included this discussion in the Supplemental Information, lines 3-28.

Line 150: Was it room air that went through the flow tube? If so, what contamination may result?

The flow tube was cleaned in between experiments with three rinses of ultrapure water with a final rinse of acetone. It was then dried with a > 99.99% purity nitrogen cylinder before being capped. Likely a small amount of room air that contains small amounts of ozone and nitrogen oxides diffuses into the flow tube during the addition of sample to the tube. However, this air would be quickly flushed from the flow tube by zero air on connection with the CIMS, and experimental data are only obtained after signals stabilize. We thank the reviewer for raising this point, and now discuss it on lines 154 as well as detail our cleaning procedure on lines ~181-185.

Line 170: What is the spectrum of the solar simulator bulbs?

We have included the solar spectrum of the solar simulator bulbs in Figure S1.

Line 177: typo

“Ion” was corrected to “Ions”

Line 189: Where is the Cl₂ background coming from? Just from chloride on flow tube or plumbing surfaces?

The signal at m/z 197 during ozone addition is not due to Cl₂ because corresponding isotopic signals at m/z 199 and 201 did not rise in concert. This has been clarified in Sect. 2.3, lines 201-203.

Line 203: I am nervous of how the HOBr sensitivity is estimated, given that the CIMS instrument is not the same as used in the referenced work by Liao et al. Wouldn't it be wiser to just call this signal uncalibrated?

On line 203-206 of the revisions, we have indicated that the HOBr signal is uncalibrated, and only discuss the relative changes in HOBr signal. Figures 3 and 4 have been adjusted to present the IHOB⁻ signals instead of the estimated mole fractions.

Response to Anonymous Referee #2

We would like to thank Anonymous Referee #2 for his/her careful reading of this manuscript and constructive suggestions. We have addressed all of his/her comments in the revised manuscript, and describe in detail changes made below in the order in which they were raised by the reviewer. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise. For clarity, the text of the reviewer's comments are in **black**, while the authors' responses are in blue.

This study reports experiments related to the photochemical halogen release from frozen sea water mimics. The results provide novel information on the halogen oxidation processes and important basis for the interpretation of field data. It becomes apparent that the most important parameters controlling halogen release are the relative proportions of chloride, bromide and iodide, pH and the structure of the frozen system, in terms of the way in which the combination of crystalline ice and brine are exposed to the gas phase. Since there is also a significant debate in the community on especially the latter two, these aspects could also be illuminated a bit better as detailed below. Overall, the experiments have been carefully designed and analysed, and the analysis of the results is associated with a proper discussion of uncertainties and related caveats (e.g., related to molecular chlorine detection in presence of ozone). The careful discussion of the halogen cycling reactions and their kinetics is appreciated. I therefore recommend this study for publication with only a few minor suggestions.

Comments:

- 1) Since the study also tries to differentiate the relative roles of photochemically produced radicals and ozone for halogen release, I wonder why no experiments have been done with ozone only for reference. While such experiments have been done in the past, indeed, exactly because of the complexity of the system in terms of microstructure, the corresponding 'ozone induced baseline dark halogen release' could have been assessed for comparison.**

Our experiments were inspired by the field work of Pratt et al. (2013) and Raso et al. (2017) that suggested evidence of photochemically-initiated halogen production, the testing of which was the primary focus of this paper. We appreciate the author's comment and acknowledge that such dark experiments with ozone only would have allowed for a more direct comparison of our results with previous laboratory experiments, such as Oum et al. (1998) and Oldridge and Abbatt (2011), discussed in our paper on lines 102-106. However, since Pratt et al. (2013) demonstrated that $O_3 + Br^-$ was relatively unimportant as a Br_2 source under normal atmospheric O_3 conditions without radiation, we focused on the role of OH as an initiator.

- 2) The authors several times discuss potential surface reactions occurring on liquid brines, I caution that diffusive exchange even over micrometer ranges is very fast, so that all halide ions present in liquid brine are available for reaction. The kinetics may indeed be limited by a surface process, but this is maybe not the important question, because as observed by the authors, it seems rather that the exchange between**

compartments may be limiting. If brine in a grain boundary is connected to the surface, diffusion is long enough to allow reaction and release within the experimental time scales. Therefore, the question remains where the less available halide ions are, if brine pockets are probably not buried below ice in such thin films. The way the films were frozen, the ice likely started to grow from the Pyrex glass walls.

We thank the Referee for this comment. The recent work from Malley et al. (2018), cited line 388) discusses the brine distribution in frozen surfaces in much more depth, and we look forward to experiments inspired by this work that will provide further clarity on this issue. But, we expect that the less-available ions are locked in the bulk ice, as discussed in lines 386-407 of the revision.

3) Could the authors please mention more precisely the irradiation conditions and how they were assessed? Has some actinometry been performed?

We have reproduced the solar irradiance spectrum of the solar simulator bulbs in Figure S1. No actinometry was performed, but we do not attempt in this paper to simulate the actual ambient radiant fluxes, but rather discuss the relative rates of production, and the roles of pH, and OH and O₃ in the gas phase on those rates.

4) pH: As the authors mention in the experimental part, this is a challenging aspect. I think a short discussion is adequate there and in the discussion section to emphasize the buffer concentrations used in relation to the halide ions, and in what way this may have affected both the physical properties and the halogen / radical chemistry.

The hydroxyl radical can react with acetic acid, as well as with bisulfate to form sulfate radical:



However, the OH reactions rates with the halides are considerably faster ($k_{\text{Cl}^-} = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{\text{Br}^-} = k_{\text{I}^-} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$). We calculate that the sulfate radical would contribute less than 0.1% to halide oxidation, compared that from OH-halide oxidation. Because this is only believed to influence the results to a minor degree, we have included the desired discussion in the Supplemental Information, Lines 3-28.

Response to Dr. Bartles-Rausch

We would like to thank Dr. Bartles-Rausch for his interest in our manuscript and for his comments. We have addressed his comments/questions below in the order in which they were raised. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise. For clarity, the text of the Dr. Bartles-Rausch comments is in **black**, while the authors' responses are in blue.

I read your manuscript with great interest and wish the best for publication in ACP. In particular, I like the increased complexity of your experiments compared to other laboratory studies and the comparison to field data.

Would you mind elaborating in more detail where you think the chemistry is occurring in your samples: the liquid fraction or the ice with its disordered interface? You clearly state that the temperature of the sample was above the eutectic of NaCl, so we can expect the presence of liquid in your system.

Based on the temperature of the experiments, and the ionic strength of the water samples used to make the ice coating, we believe the reactions occur primarily in a liquid brine on the surface of the ice layer and have clarified on lines 158-163, as well as line 2323 of the revised manuscript. This is consistent with Cho et al. (2001) and Oldridge and Abbatt (2011).

By the way, what would be the volume of liquid compared to that of ice?

Our experimental sample was 80.0 mL of an Instant Ocean solution that was made to be approximately 0.56 M with respect to NaCl (the most abundant ions in the salt). Based on simple freezing point depression thermodynamics for a 0.56M NaCl solution and an ice $T = -15^{\circ}\text{C}$, we calculate a liquid fraction of 0.124.

Then, later in the discussion the focus is placed on the disordered interface as host of the reactions - as far as I understand the manuscript. I assume you refer to the disordered interface of ice. Could you specify the role of the liquid fraction and of the ice as host for the chemistry? I think at the end this is a semantic issue, as your data are very nicely compared to studies with liquid samples (L. Artiglia, J. Edebeli, F. Orlando, S. Chen, M.-T. Lee, P. Corral Arroyo, A. Gilgen, T. Bartles-Rausch, A. Kleibert, M. Vazdar, M. A. Carignano, J. S. Francisco, P. B. Shepson, I. Gladich and M. Ammann, Nat Comms, 2017, 8, 700.) and to those with frozen samples with a considerable liquid fraction (N. W. Oldridge and J. P. D. Abbatt, J. Phys. Chem. A, 2011, 115, 2590–2598.) Indeed, Oldridge proposed that the reaction occurs in the liquid fraction of their samples.

For our analysis, we assumed that all of the chemistry occurred in the brine, as indicated on lines 158-163 and 232 of the revised manuscript.

1 **pH-Dependent production of molecular chlorine, bromine, and**
2 **iodine from frozen saline surfaces**

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25 **Abstract**

26 The mechanisms of molecular halogen production from frozen saline surfaces remain incompletely
27 understood, limiting our ability to predict atmospheric oxidation and composition in polar regions. In this laboratory
28 study, condensed-phase hydroxyl radicals (OH) were photochemically generated in frozen saltwater solutions that
29 mimicked the ionic composition of ocean water. These hydroxyl radicals were found to oxidize Cl⁻, Br⁻, and I⁻, leading
30 to the release of Cl₂, Br₂, I₂ and IBr. At moderately acidic pH (buffered between 4.5-4.8), irradiation of ice containing
31 OH-precursors (either of hydrogen peroxide or nitrite ion) produced elevated amounts of I₂. Subsequent addition of
32 O₃ produced additional I₂, as well as small amounts of Br₂. At lower pH (1.7-2.2) and in the presence of an OH
33 precursor, rapid dark conversion of I⁻ to I₂ occurred from reactions with hydrogen peroxide or nitrite, followed by
34 substantial photochemical production of Br₂ upon irradiation. Exposure to O₃ under these low pH conditions also
35 increased production of Br₂ and I₂; this likely results from direct O₃ reactions with halides, as well as the production
36 of gas-phase HOBr and HOI that subsequently diffuse to frozen solution to react with Br⁻ and I⁻. Photochemical
37 production of Cl₂ was only observed when the irradiated sample was composed of high-purity NaCl and hydrogen
38 peroxide (acting as the OH precursor) at pH =1.8. Though condensed-phase OH was shown to produce Cl₂ in this
39 study, kinetics calculations suggest that heterogeneous recycling chemistry may be equally or more important for Cl₂
40 production in the Arctic atmosphere. The condensed-phase OH-mediated halogen production mechanisms
41 demonstrated here are consistent with those proposed from recent Arctic field observations of molecular halogen
42 production from snowpacks. These reactions, even if slow, may be important for providing seed halogens to the Arctic
43 atmosphere. Our results suggest the observed molecular halogen products are dependent on the relative concentrations
44 of halides at the ice surface, as we only observe what diffuses to the air-surface interface.

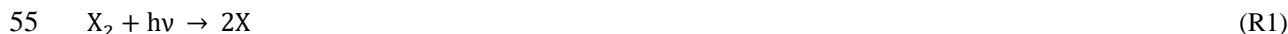
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48 1 Introduction

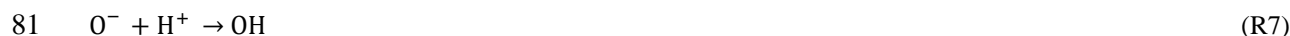
49 It is now well-established that gas-phase halogen species influence atmospheric composition through reactions
50 with ozone (O₃), volatile organic compounds (VOCs), and gaseous elemental mercury (Hg⁰) (Barrie and Platt, 1997;
51 Carpenter et al., 2013; Platt and Hönninger, 2003; Saiz-Lopez and von Glasow, 2012; Simpson et al., 2007, 2015;
52 Steffen et al., 2008, 2014, and references therein). In polar regions, it is believed that halogens build up to effective
53 concentrations through a heterogeneous reaction sequence known as the “halogen explosion” (Reactions R1-4, where
54 X represents Cl, Br, or I) (Garland and Curtis, 1981; Tang and McConnell, 1996; Vogt et al., 1996; Wennberg, 1999).



59 In this sequence, a molecular halogen (X₂) is photolyzed to produce two reactive halogen radicals. These radicals can
60 react with O₃ to produce halogen oxides (XO). The XO produced in Reaction R2 rapidly photolyzes (or reacts with
61 NO) to regenerate O₃ and X₂ in a null cycle. To irreversibly remove ambient O₃, XO must react with another halogen
62 oxide or Hg⁰. Alternatively, XO can react with HO₂ to form HOX (Reaction R3) or NO₂ to form XONO₂. Gas-phase
63 HOX can heterogeneously react with salt-laden surfaces, including sea-salt aerosol particles (McConnell et al., 1992)
64 and the “disordered interface” (often referred to as a quasi-liquid or quasi-brine layer) that exists on frozen saline
65 surfaces (Bartels-Rausch et al., 2014; Cho et al., 2002) to produce X₂, effectively returning two halogen radicals to
66 the gas phase. Additionally, this mechanism is enhanced under acidic conditions, confirmed by laboratory studies of
67 aqueous (Fickert et al., 1999) and frozen solutions (e.g., Abbatt et al., 2010; Sjostedt and Abbatt, 2008; Wren et al.,
68 2013), and from field observations (Pratt et al., 2013).

69 While much has been learned about the atmospheric chemistry of reactive halogen species in the Arctic,
70 knowledge gaps remain in the chemical mechanisms by which molecular halogens are produced from frozen surfaces
71 (Liao et al., 2014; Pratt et al., 2013). Recently, in situ, light-induced production of Cl₂ (Custard et al., 2016), Br₂ (Pratt
72 et al., 2013; Raso et al., 2017), and I₂ (Raso et al., 2017) within snowpack interstitial air has been reported, and was
73 further demonstrated to be enhanced following the addition of O₃. The Br₂-producing snowpacks studied by Pratt et
74 al. (2013) were characterized as having larger surface area, lower pH (≤ 6.3), greater [Br⁻]/[Cl⁻] molar ratios (≥ 1/148),

75 and lower salinity relative to other frozen samples collected near Utqiagvik, Alaska. The proposed mechanism for this
76 chemistry is based on laboratory studies of condensed-phase, hydroxyl radical (OH)-mediated halogen oxidation
77 (Reactions R5-R12), that is followed by partitioning of the molecular halogen to the gas phase (Abbatt et al., 2010;
78 Knipping et al., 2000; Oum et al., 1998b).



87 Direct, light-induced halogen production from frozen surfaces in the presence of OH has been previously demonstrated
88 in the laboratory for Br₂ and possibly for I₂ (Abbatt et al., 2010), but analogous chemistry for Cl₂ has yet to be observed.
89 Additionally, photochemical production of I₂ has been directly observed in the absence of OH (Kim et al., 2016).
90 Employing cavity ring-down spectroscopy, Kim et al. (2016) reported photochemical production of I₂ from a frozen
91 solution by known aqueous-phase chemistry (R13-17). This proposed photochemical mechanism involves an (I-O₂)
92 charge-transfer complex (Levanon and Navon, 1969).



98 Kim et al. (2016) also report enhanced photochemical I₃⁻ production (determined spectrophotometrically) from sunlit
99 frozen iodide solutions placed on Antarctic snowpack, as well as from refrozen field snow and glacier samples doped

100 with iodide. A question is thus raised regarding the necessity of OH for I₂ production under environmentally-relevant
101 conditions.

102 The role of O₃ in halogen production on frozen surfaces is also unclear. Previous laboratory studies have
103 demonstrated that halide-doped frozen surfaces exposed to O₃ can lead to Br₂ production (independent of radiation,
104 R18-R19, and R4) (Oldridge and Abbatt, 2011; Oum et al., 1998a; Wren et al., 2013).



107 It has recently been shown that this process proceeds at the surface, through a water-stabilized ozonide, Br·OOO⁻, as
108 shown in reactions R20-R22. Artiglia et al. (2017) observed this Br·OOO⁻ intermediate via liquid-injection X-ray
109 photoelectron spectroscopy.



113 Wren et al. (2013) found that Cl₂ was produced primarily via heterogeneous recycling of HOCl, resulting from BrCl
114 photolysis, on halide-rich artificial snow. However, the observation that O₃ induces halogen production from natural
115 frozen surfaces has yet to be confirmed by field observations of snowpack chemistry, in which exposure to only O₃ in
116 the absence of light has not been shown to produce molecular halogens (Custard et al., 2017; Pratt et al., 2013; Raso
117 et al., 2017). This raises a question of whether O₃ is more important for initial halogen release, or in a gas phase
118 propagation/recycling capacity (i.e., per the halogen explosion).

119 In this study, we utilized a custom ice-coated-wall flow reactor in tandem with chemical ionization mass
120 spectrometry (CIMS) to study Br₂, Cl₂, and I₂ production from frozen surfaces with compositions mimicking sea ice.
121 The effects of photochemically generated OH radicals, O₃ addition, and pH are tested as they relate to the production
122 of these halogens. Surface pH was controlled through use of buffers.

123 2 **Methods**

124 **2.1 Materials**

125 Sample solutions were composed to mimic the halide composition of seawater. This was achieved using
126 either dissolved Instant Ocean (Spectrum Brands), or commercially available halide salts at a composition that mimics
127 Instant Ocean (for consistency) in solutions referred to hereafter as “saltwater.” The halide concentrations in these
128 solutions were made to a final concentration of 0.56M Cl⁻, 7.2 x 10⁻⁴ M Br⁻, and 1.9 x 10⁻⁶ M I⁻. Except for Instant
129 Ocean, all chemicals were purchased from Sigma Aldrich. Halide salts include solid NaCl (puriss. p.a. grade, ≥99.5%
130 purity), NaBr (puriss. grade, >99% purity), KI (puriss. p.a. grade, ≥99.5% purity). We note that these halide
131 concentrations are comparable to those in actual seawater (Herring and Liss, 1974; Luther et al., 1988; Tsunogai and
132 Sase, 1969), which typically contains Cl⁻, Br⁻, and I⁻ at ratios of 1:^{1/660}:^{1/200,000}. Solutes were dissolved in ultrapure
133 water (Birck Nanotechnology Center). Dissolved organic carbon for Instant Ocean and halide salt solutions were
134 analyzed using a Shimadzu TOC-V_{CSH} Total Organic Carbon Analyzer, and determined at approximately 70 mg/L for
135 Instant Ocean solutions, and less than 5 mg/L for saltwater solutions. No further characterization of carbon-containing
136 compounds was performed.

137 While previous investigators have adjusted the pre-freezing pH of their samples, it is very difficult to know
138 the pH in the surface brine (or disordered interface) of frozen samples (Bartels-Rausch et al., 2014), though there is
139 evidence from laboratory studies suggesting that the pH of salt solutions remains largely unchanged after freezing
140 (Wren and Donaldson, 2012b). To obviate this problem, the aqueous solutions used in this study were buffered so
141 that the same pH should exist in the surface brine layer. All solutions were buffered by either a 20 mM acetic acid
142 (ACS reagent grade, ≥99.7% purity)/acetate (puriss. p.a. grade) buffer (pH ≈ 4.5-4.7), or a 20 mM bisulfate
143 (ReagentPlus grade, 99% purity)/sulfate (ReagentPlus grade, ≥ 99.0% purity) buffer (pH ≈1.7 – 2.2). These buffer
144 concentrations were chosen as a compromise between using as little buffer as possible, yet enough buffer to ensure
145 adequate buffering ability, as buffer capacity rapidly decreases as constituent species concentrations approach the acid
146 K_a value. pH values of sample solutions were determined before and after experiments with no significant changes
147 observed, suggesting the buffer composition/buffering capacity does not appreciably change over the course of an
148 experiment (discussed further in the Supplemental Information). 100 μM of either hydrogen peroxide (trace analysis

149 grade, $\geq 30\%$ purity) or sodium nitrite (ReagentPlus grade, $\geq 99.0\%$ purity) were included as photochemical hydroxyl
150 radical precursors, via reactions R5, and R6-7.

151 2.2 Flow tube

152 Experiments were performed in a custom-built 150 cm long, 2.5 cm ID frozen-walled Pyrex flow tube
153 contained within a temperature-controlled cooling jacket. In each experiment, 80.0 mL of sample solution was poured
154 into the tube **in the presence of room air**, which was subsequently sealed with vinyl caps (McMaster-Carr). The flow
155 tube was then rotated on motorized rollers within a 170 cm x 50 cm x 50 cm, insulated wooden cooling chamber.
156 Crushed dry ice was placed along the bottom of the chamber, and fans were used to circulate the air throughout the
157 chamber such that the flow tube was evenly cooled. After ~ 30 minutes, the sample was evenly frozen (ice thickness
158 of 0.9 mm). The flow tube was subsequently transferred to an enclosed 156 cm x 50 cm x 50 cm wooden, Mylar-
159 lined experiment chamber, and connected to a recycling chiller set to 258 K (i.e., above the $\text{NaCl}\cdot 2\text{H}_2\text{O}$ eutectic point,
160 in which the relevant chemical reactions are expected to occur with / in a brine on the ice surface (Cho et al., 2002;
161 Oldridge and Abbatt, 2011)). This conjecture is based on the work of Oldridge and Abbatt (2011), who reported from
162 a series of similar experiments that when O_3 is flowed over frozen NaCl/NaBr solutions above the NaCl eutectic
163 temperature, reaction kinetics were strongly consistent with chemistry occurring in a liquid brine. The cooling liquid
164 used for the chiller was a mixture of 60% ethylene glycol and 40% distilled water. Six UVA-340 solar simulator
165 lamps (Q-Lab, 295 – 400 nm with maximum wattage at 340 nm, **irradiance spectrum in Fig. S1**) were installed in the
166 experiment box (two on each side except bottom). Each side was lined with reflective Mylar sheets to evenly irradiate
167 the flow tube when the lamps were powered.

168 A flow schematic representing typical experiments is shown in Fig. 1. The carrier gas (Air, Ultra Zero grade,
169 Praxair) was scrubbed of volatile organic compounds using activated charcoal, and water by travelling through coiled
170 stainless-steel tubing surrounded by crushed dry ice (replaced throughout the course of an experiment). This gas was
171 measured to contain $\leq 300 - 400 \text{ pmol mol}^{-1}$ NO (experimentally determined limits of detection) using the Total
172 REactive Nitrogen Instrument (TRENI) (Lockwood et al., 2010; Xiong et al., 2015). Though NO_2 was not measured,
173 it should have been removed by the charcoal trap. Before entering the coated-wall flow tube, the carrier gas flowed
174 through a commercial O_3 generator (2B Technologies model 306). Carrier gas air entered the tube near room
175 temperature (20 °C). At the start of experiments, the O_3 generator was set to 0 nmol mol^{-1} . Carrier gas then entered

176 the flow tube in the dark experiment chamber. In most experiments, the carrier gas was regulated to a volumetric flow
177 rate of 4.0 L min⁻¹, which yields a residence time in the flowtube of ~12 seconds. On exiting the flow tube, sample
178 air was characterized using a Thermo Environmental 49i O₃ monitor (flow rate of ~1.5 L min⁻¹) and a chemical
179 ionization mass spectrometer (CIMS, sampling flow rate of ~1.7 L min⁻¹, described below in Sect 2.3). Excess flow
180 air was vented away. At set times in an experiment, the solar simulator bulbs were activated, and O₃ was added to the
181 system by powering the O₃ generator. At the end of each experiment, the ice was melted and the water collected for
182 pH measurements. To clean the flow tube, its interior was washed three times with ultrapure water before a final rinse
183 with wash acetone. The flow tube was then connected to a compressed nitrogen gas cylinder (Praxiar, >99.99% purity)
184 to dry for at least 2 hours. Once dry, the flow tube was disconnected and capped until the next experiment.

185 2.3 CIMS

186 Halogen species were detected using a chemical ionization mass spectrometer (CIMS), described previously
187 by Liao et al. (2011) and Pratt et al. (2013). Chemical ionization is achieved by ion-molecule reactions that occur
188 between iodide-water reagent clusters, I(H₂O)_n⁻ in N₂, and the gas-phase analytes in zero air. The iodide-water clusters
189 are formed when gas-phase iodide ions, generated by flowing 5 ppm methyl iodide through a ²¹⁰Po ionizer (NRD)
190 combines with water in the humidified ion-molecule region of the CIMS. Ion were filtered using a quadrupole mass
191 filter. The ice-coated flowtube was connected to the CIMS via approximately 50 cm of i.d. 1/2" PFA Teflon tubing.

192 A typical CIMS sampling cycle consisted of an 8.35s duty cycle. Dwell times for all monitored species were
193 250 ms except for the reagent ion (detected as *m/z* 147, I(H₂¹⁸O)⁻), which was set to a dwell time of 100 ms. The 18
194 ions analyzed in this study are listed in Table 1, but we focus herein on results concerning masses related to Br₂ (*m/z*
195 285 and 287: I⁷⁹Br⁷⁹Br⁻ and I⁸¹Br⁷⁹Br⁻, respectively), Cl₂ (*m/z* 197, 199, and 201: I³⁵Cl³⁵Cl⁻, I³⁷Cl³⁵Cl⁻, and I³⁷Cl³⁷Cl⁻),
196 and I₂ (*m/z* 381: I₃⁻). In addition, IBr (*m/z* 333 and 335: I⁷⁹IBr⁻, I⁸¹IBr⁻) was unambiguously detected in some
197 experiments. The presence of Br₂, Cl₂, and IBr was confirmed by measuring the ratios between the two isotope signals
198 for each mass, compared to the natural abundances (i.e., 1.95 for *m/z* 287:285; 1.54 for *m/z* 197:199; and 1.03 for *m/z*
199 333:335, respectively). Data outside ±25% the expected isotope ratio were excluded from analysis. The signals for
200 BrCl (*m/z* 241 and 243: I⁷⁹Br³⁵Cl⁻, I⁸¹Br³⁵Cl⁻, I⁷⁹Br³⁷Cl⁻) masses were never observed at the correct ratios (1.3 for *m/z*
201 243:241), and so those data were not reported here. As the introduction of ~60 nmol mol⁻¹ O₃ to the experimental
202 system significantly increased the baseline signal of *m/z* 197, but not *m/z* 199 or 201, the presence of Cl₂ could not be

203 confirmed under elevated O₃ conditions. In addition, background subtracted, relative signals for *m/z* 271 (IHOI⁻) and
204 *m/z* 225 (IHO⁸¹Br⁻) are discussed (signals are relative to that of the ionization gas (*m/z* 147, I(H₂¹⁸O))). According to
205 isotope ratios, IHOBr⁻ was not unambiguously observed, however, due to an interference at *m/z* 223 (IHO⁷⁹Br⁻), and
206 our results here should be considered for only qualitative purposes as we only discuss relative changes in the signal.

207 CIMS calibrations were performed using I₂, Br₂, and Cl₂ permeation devices (VICI) at the start and
208 conclusion of each experiment. Br₂ and Cl₂ permeation outputs were quantified using the spectrophotometric method
209 described by Liao et al. (2012). The I₂ permeation output was quantified by flowing the I₂ through an impinger
210 containing a NaHCO₃ (30mM)/NaHSO₃ (5mM) reducing solution. This solution quantitatively reduces I₂ to I⁻, which
211 was then determined using a Dionex DX500 ion chromatography system. Permeation rates were calculated for each
212 experiment and found to average (1.9±0.1) × 10⁻¹¹, (5.5±0.1) × 10⁻¹⁰, and (8.6±0.1) × 10⁻¹⁰ mol min⁻¹ of I₂, Br₂, and
213 Cl₂, respectively (uncertainties representing standard error of the mean). CIMS calibration factors were calculated for
214 individual experiments. These factors are based on the average of the signal sensitivities, determined from the
215 permeation sources, calculated at the start and completion of each experiment. Corresponding uncertainties for these
216 calibration factors thus represent the 1σ standard deviation of the mean sensitivity. An approximate I⁷⁹IBr⁻ calibration
217 factor was assumed to be the average of the sensitivities for *m/z* 287 (IBr₂⁻) and 381 (I₃⁻). Background measurements
218 were performed before and after the experiment (minimum of 5 min) by passing the carrier gas through the
219 experimental flow tube (without O₃, in the dark), and subsequently through a glass wool scrubber, previously shown
220 to remove molecular halogens with greater than 95% efficiency (Liao et al., 2012; Neuman et al., 2010). Temporal
221 variations in bromine-species signals while using the low pH sulfate/bisulfate buffer were observed in some
222 experiments (Fig. S2) and are discussed in the Supplementary Information.

223 Analysis of experimental data was based on one-minute averages, with uncertainties representing the
224 standard deviation of these averages. Subsequently, signals were converted to concentrations using the sensitivities
225 calculated above, propagating the sensitivity uncertainty into the measurement uncertainty. Average limits of
226 detection (3σ) across all experiments for the molecular halogens during background periods were 1.8 ± 0.4, 1.2 ± 0.3,
227 and 9 ± 2 pmol mol⁻¹ for Br₂, Cl₂, and I₂ respectively (uncertainties representing standard error of the mean).
228 Additionally, reported uncertainties for integrated amounts of formed halogens are calculated as integrated halogen
229 concentrations multiplied by the relative uncertainty in the CIMS signal sensitivity.

230 3 Results and Discussion

231 The experiments described here address the extent to which condensed-phase OH radicals **in an ice surface brine**
232 (Cho et al., 2002) can produce I₂, Br₂, and Cl₂ through condensed-phase reactions within frozen saline surfaces, as
233 hypothesized by recent field (Custard et al., 2017; Pratt et al., 2013; Raso et al., 2017) and laboratory experiments
234 (Abbatt et al., 2010). In addition, we test the pH-dependence of this chemistry and whether gas-phase O₃ enhances
235 this production. We find the relative and absolute amounts of halogens produced from ice are a complex function of
236 the relative concentrations of the precursor halide ions, pH, presence of oxidants, radiation, and O₃.

237 The ice-coated flow tube experiments started under dark conditions and without addition of O₃ (Sect. 3.1). Once
238 signals stabilized, lights were activated (Sect. 3.2). After 1-2 hours, ~60 nmol mol⁻¹ of O₃ was introduced into the
239 carrier gas (Sect. 3.3). Integrated amounts of produced molecular halogens are presented in Table 2 for all
240 experiments. Unless otherwise specified, integrated amounts of produced halogens represent amounts produced over
241 the course of 1 h of exposure to light (Sect. 3.2) and/or ozone (Sect. 3.3). Saline ices tested include frozen Instant
242 Ocean (IO) solutions, “saltwater” (SW) solutions composed of dissolved reagent grade salts mimicking seawater
243 composition, and 0.56 M high purity NaCl (CL1). OH-radical precursors used include hydrogen peroxide (H₂O₂) or
244 nitrite (NO₂⁻), which have been estimated to account for 96% of snowpack photochemical OH formation at Utqiagvik,
245 AK (France et al., 2012). Many of the salient features of our results are demonstrated by example experiments shown
246 in Fig. 2, including the impact of irradiation in the presence of ice phase OH radical precursors, varied pH, and the
247 presence of O₃. Below we discuss the results and interpretations of our experiments, organized by the mechanism of
248 halogen production and halogen products themselves.

249 3.1 Dark reaction production of I₂

250 After the initial connection of the flowtube to the CIMS (i.e., before irradiation or addition of O₃), large I₂
251 signals (measured as I₃⁻, *m/z* 381) were observed in several cases where OH-radical precursors were utilized, especially
252 when pH ≤ 2 (e.g., Fig. 2b, Fig. S2). Integrated calibrated sums of this dark I₂ production are estimated in Table S1,
253 and span from the time when the flowtube was connected to the CIMS until lights were activated. When pH ≤ 2, dark
254 production of I₂ sometimes caused significant depletion of reservoir I⁻. Experiments IO4 and SW5 (both using H₂O₂
255 as an OH precursor) only had, at most, ~36% of the initial 152 nmol of I⁻ by the time lights were turned on (remaining
256 I⁻ was estimated by subtracting twice the observed I₂ (i.e., two I⁻ for every I₂) from the initial 152 nmol of I⁻ in the IO

257 or SW solutions). Considerably less dark I₂ production occurred using NO₂⁻ as an OH precursor (depleting I⁻ by an
258 average of 4.5%, Table S1). However, the amounts in Table S1 represent lower limits of the dark-produced I₂; it is
259 impossible to accurately determine the extent of dark I₂ production since some was lost from the flow tube during its
260 connection to the CIMS after freezing (Fig. 1). At pH ≈ 4.7, this production was relatively modest. Only experiment
261 IO2 was noticeably affected, in which only ~0.5% of initial I⁻ was removed by dark mechanisms (Table S1). Under
262 both pH regimes (i.e. ~4.7 and < 2), this signal subsequently decayed as I₂ flushed out of the system until reaching a
263 low steady state concentration. No corresponding dark production of Br₂ or Cl₂ was observed for any experiments at
264 any pH.

265 As previously reported, both H₂O₂ and NO₂⁻ can directly convert I⁻ to I₂ under dark acidic conditions. The
266 oxidation of I⁻ by H₂O₂ occurs through the condensed phase reactions R23 and R24 (Küpper et al., 1998):



269 Nitrite ions react with hydronium ions to form the nitroacidium ion, H₂ONO⁺, which has been previously shown to
270 produce I₂ (R25-R27) (Hellebust et al., 2007; O'Driscoll et al., 2006, 2008; O'Sullivan and Sodeau, 2010):



274 Therefore, it is likely the I₂ observed on connection of the flowtube to CIMS originated from the above reactions
275 (R23-27), as the pH ≤ 2 experiments in this work (IO3-5, SW3-5) favor these forward reactions.

276 **3.2 Hydroxyl radical-induced halogen production**

277 **3.2.1 pH ≈ 4.7**

278 At pH ≈ 4.7, frozen solutions without OH radical precursors produced no (IO6, SW6-SW7) or little (IO7,
279 0.10 ± 0.06 nmol of I₂) amounts of molecular halogens above their respective LODs after activation of lights (Table
280 2). The small amount of I₂ produced in IO7 possibly originates from the light and O₂-mediated production mechanism
281 proposed by Kim et al. (2016) as summarized within R13-R17. However, as shown below, this mechanism of I₂
282 production is of relatively minor importance at this pH.

283 In the presence of H_2O_2 at $\text{pH} \approx 4.7$, I_2 mole fractions increased rapidly upon irradiation, as shown in Fig. 2a.
284 Of the four experiments performed in these conditions (IO1, IO2, SW1, SW2), three experiments (IO1, SW1, SW2)
285 produced statistically similar amounts of I_2 (mean: 8 ± 2 nmol) after one hour of irradiation (Table 2). The I_2 signal
286 behavior in Experiment IO2 qualitatively shared the same features as Experiments IO1, SW1, and SW2 (Fig. S3), but
287 provided an apparently statistically different amount of I_2 ($0.6 (\pm 0.4)$ nmol) based on the objectively chosen integration
288 limits. This experiment is discussed further in the Supplemental Information.

289 Regarding other molecular halogens, IBr was observed above the estimated limits of detection (3 pmol
290 mol^{-1}) upon irradiation during Experiment SW2 (Fig. 2a), starting approximately 20 minutes before the addition of
291 O_3 . No photochemically produced (OH-induced) Br_2 was unambiguously observed at this pH (note that the apparent
292 IO2 Br_2 production of 0.034 ± 0.003 nmol is likely overestimated and discussed in more detail in the Supplemental
293 Information). Cl_2 mole fractions remained below limits of detection in all cases with OH-precursors at this pH.

294 3.2.2 $\text{pH} \leq 2$

295 In cases without OH precursors at $\text{pH} \leq 2$, photochemical I_2 production was observed (integrated production
296 of 14 ± 10 nmol for IO8, and 6 ± 2 nmol for SW8) (Table 2), contrasting with experiments performed at $\text{pH} \approx 4.7$ in
297 which very little was produced. This production likely stems from the mechanisms outlined by Kim et al. (2016)
298 (R13-17), which requires only light and oxygen to form a charge-transfer complex that results in I_2 production
299 (discussed in Sect. 1). Molecular Br_2 and Cl_2 concentrations remained below limits of detection, consistent with
300 Abbatt et al. (2010), in which no Br_2 or Cl_2 was observed without an OH-precursor.

301 As discussed in Sect. 3.1, inclusion of H_2O_2 or NO_2^- can result in direct oxidation of I^- and reduce the available
302 $[\text{I}^-]$ for photochemical OH oxidation when $\text{pH} \leq 2$. Photochemical production of I_2 across experiments yielded ≤ 0.82
303 nmol (IO4, IO5, and SW5) when H_2O_2 was used as an OH precursor. However, when instead NO_2^- was used (as in
304 IO3, SW3, and SW4), initial observations of I_2 on flowtube connection to CIMS were as much as 90% less than when
305 H_2O_2 was used (Table S1), thereby leaving more I^- available for reaction. For experiment IO3 (using NO_2^-), the
306 reduced pH led to an observed photochemical I_2 production amount of 39 ± 1 nmol, approximately four times larger
307 than the largest amount observed at $\text{pH} \approx 4.7$ (9 ± 3 nmol, Table 2). That production would be enhanced at lower pH
308 was expected based on the halogen activation reactions R4-R22. The corresponding “saltwater” experiments using
309 NO_2^- were not as conclusive; experiment SW3 only yielded 4.0 ± 0.1 nmol of photochemical I_2 (Fig. S5). Experiment

310 SW4 (a repeat of SW3) did not produce any photochemical I₂ and qualitatively resembles the H₂O₂ experiments
311 performed at this pH. It is possible that, for SW3 and SW4, more I₂ was produced by dark reactions and flushed out
312 of the tube during connection with the CIMS and therefore would not have been measured.

313 Photochemical production of Br₂ does not appear until I₂ production decreases. The results shown in Figures
314 2a and 2b demonstrate that when [I⁻]/[Br⁻] approximates the initial conditions of Instant Ocean (~2.6 x 10⁻³), OH-
315 mediated I₂ production precedes Br₂ and IBr production (as in the pH ≈ 4.7 experiments and IO3, in which significant
316 dark I₂ production was not observed). After [I⁻]/[Br⁻] has sufficiently decreased, Br₂ eventually becomes the dominant
317 photochemical product. As demonstrated by experiment IO4 (Fig 2b and inset), there is a delay in Br₂ production
318 until I⁻ was removed as I₂, then as IBr. For experiments that used H₂O₂, photochemical Br₂ yields averaged 4.5 ± 0.5
319 nmol between IO4 and IO5, and 6.0 ± 0.7 nmol from SW5. Experiment SW4 (using NO₂⁻) produced a comparable
320 amount of Br₂ (5.4 ± 0.7 nmol). Given the initial depletion of I⁻ from dark I₂ production (Sect. 3.1), we can estimate
321 [I⁻]/[Br⁻] at pH ≤ 2 in ice with H₂O₂ just before irradiation based on the remaining moles of I⁻ in solution (Table S1)
322 and the total moles of Br⁻ in the solution. Averaging values from Experiments IO4-5 and SW5, [I⁻]/[Br⁻] was calculated
323 as (1.6 ± 0.7) x 10⁻⁴ (compared to the initial ratio of 2.6 x 10⁻³) and was sufficiently low to result in photochemical
324 production of Br₂.

325 Photochemical Cl₂ production was only observed from a frozen solution of “pure” 0.56 M NaCl and H₂O₂ at
326 pH=1.8 (CL1), as shown in Fig. 2c. The initial Br⁻ impurity of this CL1 solution was determined to be (4.5 ± 0.3) x
327 10⁻⁶ M via ion chromatography, while any I⁻ impurity concentration could not be detected above the 3σ LOD of 90
328 nM. When the lights were turned on, slight increases in I₂ and IBr were observed in concert with a rapid rise in Br₂.
329 After about one hour of apparent equilibrium, I₂ concentrations began decreasing, while Br₂, IBr, and Cl₂ continued
330 rising. Over one hour of illumination, 93 ± 3 pmol of Cl₂, 100 ± 10 pmol of Br₂, and 100 ± 10 pmol of I₂ were observed.
331 However, as shown in Fig 2c, the greatest rate of increase in Cl₂ signal occurred just after this time. Integrating instead
332 from t=0 until t=2 hours, the amount of Cl₂ produced was 190 ± 10 pmol, while the amount of Br₂ increased to 310 ±
333 20 pmol. Utilizing the starting halide concentrations of Br⁻ and Cl⁻ for CL1, our results show Cl₂ production was
334 observed at [Br⁻]/[Cl⁻] of 8.1 x 10⁻⁶ (1/124,000), compared to the Instant Ocean [Br⁻]/[Cl⁻] of ~ 1/800. Unfortunately, BrCl
335 could not be observed due to an unknown interference at m/z 241 and 243.

336 The observations in this study indicate competition for the OH radical in which the most oxidizable halide is
337 oxidized, and the corresponding molecular halogens are produced until that halide ion is depleted in the ice surface

338 brine reaction environment. The trends in molecular halogen production confirm acid-enhanced mechanisms in which
 339 the dominant products are largely dependent on relative halide ratios. Here, Br₂ and IBr were not observed until I₂
 340 production sufficiently decreased the [I⁻]/[Br⁻] ratio, and Cl₂ was not observed unless the [Br⁻]/[Cl⁻] ratio was
 341 sufficiently low ([Br⁻]/[Cl⁻] = 8.1 x 10⁻⁶, as discussed above). This observation is consistent with Sjostedt and Abbatt
 342 (2008), who exposed frozen salt solutions to gas-phase OH and found peak BrCl production occurred as Br⁻ decreased
 343 from an initial [Br⁻]/[Cl⁻] of 7.3 x 10⁻⁵. Additionally, Abbatt et al. (2010) generated condensed phase OH on frozen
 344 surfaces via the photolysis of nitrate, and similarly found lower Br₂ and IBr integrated amounts at lower [Br⁻]/[Cl⁻]
 345 when temperatures were higher than the eutectic point of sodium chloride. These halide ratios are also consistent with
 346 in situ snowpack observations of Br₂, BrCl, and Cl₂ formation (Custard et al., 2017; Pratt et al., 2013).

347 **3.2.3 Relative Reactivities of OH-induced Halogen Production**

348 I₂, Br₂, and Cl₂ have been previously observed at mole fractions within less than two orders of magnitude of
 349 each other in snowpack interstitial air at Utqiagvik, AK, (Custard et al., 2017; Raso et al., 2017). Custard et al. (2017)
 350 observed gas phase [Br₂]/[Cl₂] values for artificially irradiated, acidic snowpacks ranging from 2-95 for corresponding
 351 snowpack [Br⁻]/[Cl⁻] ratios of (6 ± 1) x 10⁻⁴. Under similar conditions, Raso et al. (2017) observed [I₂]/[Br₂] ranging
 352 from ~0.4-0.8 from corresponding snowpack [I⁻]/[Br⁻] amounts of (2.6±0.6) x 10⁻³. Despite the large differences in
 353 relative halide abundance (i.e., [I⁻] << [Br⁻] << [Cl⁻]), it appears that halogen activation reaction kinetics favor the
 354 larger halide ions, effectively levelling the relative molecular halogen production rates. The observations herein
 355 provide an opportunity to explore the relative reactivities of OH-mediated halogen production.

356 If we assume that the observed X₂ flux out of the ice is proportional to the production rate (i.e., X₂ desorbs
 357 as it is produced, within the residence time of the flow tube) and that halogen production is limited by halide reaction
 358 with OH radicals, effective relative reactivities, k_X/k_Y, (where X and Y represent Br, Cl, or I) can be calculated using
 359 Eq. 1.

$$360 \frac{\text{Flux}_{X_2}}{\text{Flux}_{Y_2}} = \frac{k_{X^-}[X^-][OH][H^+]}{k_{Y^-}[Y^-][OH][H^+]} \quad (1)$$

361 The initial molecular halogen flux is calculated as the integrated sum of X₂ (in moles) divided by both integration time
 362 (t = 0-3 minutes, starting from the beginning of irradiation) and the surface area of ice coverage in the flow tube.
 363 Because the surface area, as well as the [OH] and [H⁺] in the ice surface reaction environment, are identical within

364 individual experiments and cancel in these calculations the relative fluxes are simply equivalent to the relative outflow
365 concentrations of halogens. The pre-freezing halide ion concentrations (defined in Sect. 2) thus allow us to solve for
366 the effective relative reactivity, k_X/k_Y , by assuming the ratios of the halide ice concentrations are the same after
367 freezing.

368 At $\text{pH} = 1.8$, $k_{\text{Br}^-}/k_{\text{Cl}^-}$ was estimated to be $(2.4 \pm 0.2) \times 10^5$ from experiment CL1; in other words, production
369 of Br_2 is 240,000 times more efficient than production of Cl_2 via $(\text{OH} + \text{halide})$ in the surface layer. Across the six
370 experiments performed at $\text{pH} \leq 2$ (average of 1.85) using Instant Ocean (IO3, IO4, IO5) and saltwater (SW3, SW4,
371 SW5), $k_{\text{I}^-}/k_{\text{Br}^-}$ was calculated to average $(9 \pm 4) \times 10^3$ (reported uncertainty is the standard error of the mean, and thus
372 only represents the experiment repeatability). These relative reactivities are substantially larger than the
373 corresponding relative aqueous $\text{OH} + \text{halide}$ rate constants ($k_{\text{I}^-} = k_{\text{Br}^-} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988; Zehavi
374 and Rabani, 1972), $k_{\text{Cl}^-} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Grigor'ev et al., 1987)), which are different by less than a factor of 4.
375 However, these rate constants refer to the specific fundamental reaction of OH with X^- to produce HOX , as in Reaction
376 R8. Ultimately, X_2 production would occur via R8-R12, and this condensed phase chemistry is much more complex
377 when also considering interhalogen reactions, such as R28, that involve combinations of the three molecular halogens,
378 halides, and mixed molecular halogens (XY , where $\text{Y} = \text{Cl}, \text{Br}, \text{or I}$).



380 Thus, it must be that there exist competing reactions that make the production of the larger X_2 more efficient. For
381 example, $\text{Cl} + \text{I}^- \rightarrow \text{ClI}^-$ may be faster than $\text{Cl} + \text{Cl}^- \rightarrow \text{Cl}_2^-$. Alternatively, the relative rates of the disproportionation
382 reaction R11 are likely different, favoring the larger molecular halogens. We can thus only state from these
383 observations that the apparent relative reactivities calculated are consistent with the overall reactivity of the larger
384 ions compensating for their lower abundances. This may lead to comparable production rates in our laboratory
385 experiments and comparable snowpack gas phase concentrations.

386 The above relative reactivity calculations are considered upper limits since the halide ratios used represent
387 those in the pre-freezing solution. In other words, it is assumed that the ions are excluded to the ice surface reaction
388 environment-air interface in amounts proportional to their pre-freezing concentration. Malley et al. (2018) recently
389 demonstrated that brine can be distributed throughout ice in channels, suggesting that only the solutes at the liquid-air
390 interface (a fraction of the total pre-freezing solution) participate in heterogeneous chemistry. Indeed, we find

391 evidence here suggesting not all ions are available for reaction at the ice brine surface, particularly for experiments
392 for which little I⁻ was lost from dark I₂ production mechanisms (i.e., pH = 4.7 with OH precursors: IO1, IO2, SW1,
393 SW2). Considering experiment IO2 as an example (Fig. S5; pH = 4.7), integration of the I₂ signal during ~15 hours
394 of exposure to both light and O₃ shows that 54% (82 nmol) of the original 152 nmol of I⁻ remained unreacted in the
395 frozen solution despite the signal apparently stabilizing at its baseline. It is therefore probable that a significant number
396 of the ions, as well as H₂O₂, exist within brine channels within the ice (Bartels-Rausch et al., 2014; Malley et al.,
397 2018). Oxidation chemistry would then be occurring throughout the ice, but release of molecular halogens to the flow
398 tube air would be determined by diffusion rates. The diffusion rates of the product molecular halogens through bulk
399 ice are likely slow, such that only production occurring in the brine that is in the near-liquid-air interface is observed
400 here (Abbatt et al., 2012). Of the halogens produced from frozen solutions here, it is expected that I₂ is observed most
401 readily given the high polarizability and surface affinity of I⁻ in aqueous solutions (Gladich et al., 2011), and the
402 relative ease of oxidation of I⁻. That is, surface concentrations will be relatively enhanced with larger, more polarizable
403 anions (I⁻ > Br⁻ > Cl⁻) (Gladich et al., 2011), which favors production of I₂ over Br₂, and Br₂ over Cl₂. As the
404 larger/more reactive ions are depleted through oxidation, the next largest ion then becomes more favorably oxidized.
405 Thus, in addition to the impact of differential reactivities and competing reactions for R9-R12, what we observe in the
406 laboratory and in the field can also be influenced by the relative surface enhancements of the anions, especially with
407 respect to O₃ impacts as discussed below.

408 3.3 Effects of O₃ on halogen production

409 In experiments without an OH source (IO6-IO8, SW6-SW8), I₂ production was greatest when O₃ was
410 introduced to the irradiated tube for both pH regimes (Table 2). The amount of I₂ produced over 60 minutes in these
411 experiments was large, ranging from 26 ± 9 nmol to 80 ± 1 nmol at pH = 4.7, and from 2.6 ± 1.7 nmol to 38 ± 12 nmol
412 at pH < 2. This production likely results from a combination of heterogeneous recycling, and the surface and aqueous
413 reactions between O₃ and I⁻ ($k = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Liu et al., 2001)). While the I₂ produced when pH <
414 2 appears to be lower, I₂ had already been produced in the presence of light prior to addition of O₃ (Sect. 3.2.2),
415 yielding a lower [I⁻]/[Br⁻] ratio when O₃ was eventually added. Br₂ production amounts ranged from 0.012 ± 0.001
416 nmol to 0.16 ± 0.01 nmol at pH = 4.7 and taking up to 6 hours to raise above detection limits after O₃ was added. At
417 pH ≤ 2, Br₂ production amounts ranged 0.14 ± 0.02 nmol to 0.93 ± 0.05 nmol. While O₃-mediated halogen production

418 has been observed directly from frozen surfaces in the absence of light in previous laboratory studies (Artiglia et al.,
419 2017; Oldridge and Abbatt, 2011; Oum et al., 1998a; Wren et al., 2013), Br₂ production has not been directly observed
420 from the Arctic snowpack without irradiation (Pratt et al., 2013). This raises a question of the role of O₃ in initial
421 halogen release in the Arctic spring.

422 When OH-precursors were present, the addition of O₃ to the zero-air flow over the irradiated frozen sample
423 caused additional production of I₂ and Br₂, as shown in Figure 2a and b, under both pH regimes (Table 2). In
424 experiments at pH ≈ 4.7 in which [I⁻]/[Br⁻] remained sufficiently large due to minimal dark production of I₂ (i.e., IO1-
425 2, SW1-2), exposure to O₃ caused a sharp increase in I₂ (as in Fig. 2a). I₂ production amounts for frozen Instant Ocean
426 at pH ≈ 4.7 (IO1, IO2) averaged 22 ± 10 nmol, about two times less than for frozen saltwater experiments SW1 and
427 SW2 (average production amount of 51 ± 25 nmol). As the I₂ signal decayed, the corresponding Br₂ signals gradually
428 increased above detection limits, approximately 3h after the introduction of O₃ (Fig. 2a). The average integrated
429 amounts of Br₂ produced from these pH ≈ 4.7 experiments were very similar (0.05 ± 0.01 nmol for IO experiments
430 and 0.03 ± 0.01 nmol for SW experiments).

431 When pH < 2, the effects of O₃ addition varied according to the remaining availability of I⁻. When the surface
432 I⁻ reservoir had been reduced from dark reactions with H₂O₂ or NO₂⁻ (R17-21; Sect. 3.1), exposure to O₃ did not
433 increase I₂ above the LOD except in experiment IO5, which exhibited a small spike before decaying below the LOD
434 (0.11 ± 0.06 nmol in IO5). However, O₃ did cause additional Br₂ production after one hour (average of 10 ± 2 nmol
435 for IO4 (Fig. 2b) and IO5 (Fig S4), and 14 ± 2 nmol for SW4 and SW5). In contrast, for SW3 (using NO₂⁻ as an OH
436 source), there was relatively little initial consumption of I⁻ by dark reaction; therefore, when O₃ was added, 1.1 ± 0.1
437 nmol additional I₂ was observed, comparable to what was observed with the higher pH experiments (Fig. S5). The
438 amount of Br₂ produced (0.46 ± 0.01 nmol) was also significantly less than observed when I⁻ was initially depleted,
439 demonstrating the importance of the halide ratios.

440 This additional O₃-induced halogen production could result from a combination of mechanisms. First, as
441 discussed above, O₃ can react with halides on frozen saline surfaces to produce Br₂ or I₂ per reactions R18-19, and
442 then R4 (Artiglia et al., 2017; Carpenter et al., 2013; Gladich et al., 2015; Hayase et al., 2010; Oum et al., 1998a;
443 Shaw and Carpenter, 2013; Wren et al., 2013). It is possible that Br₂ (as well as other halogens) may have been
444 produced via this mechanism at levels below the LOD in previous Arctic snowpack studies (Custard et al., 2017; Pratt
445 et al., 2013; Raso et al., 2017).

446 The presence of O₃ also yielded HOX compounds (Fig. 3-4), likely formed in the flowtube in part by O₃
447 reactions with halides (R18-R19). Additionally, given a flow tube residence time of 12 seconds, gas phase production
448 of HOX is possible via R1-R3 and could act as an additional X₂ production source (via R4), given a timescale for
449 molecular diffusion of 6.5 seconds for HOBr from the center of the tube to the ice surface. At this flow rate, there is
450 enough time for 1-2 heterogeneous reaction cycles. Figure 3 shows HOX for IO₂ (pH=4.7 with H₂O₂ present,
451 analogous to IO₁, SW1, SW2). For each experiment in this series, increases in I₂, HOI, and Br₂ were readily observed
452 when the O₃ was introduced at hour 2 (Fig. 3, Fig. S4). However, corresponding HOBr production was not observed,
453 perhaps either due to a high LOD, or the relatively low abundance of Br₂ that would limit production of HOBr.
454 Conversely, in pH ≤ 2 cases when substantial portions of I⁻ had already reacted prior to irradiation (IO₄, IO₅, SW₄,
455 SW₅), the addition of O₃ produced negligible amounts of I₂ and HOI (Fig. 4). But, in these cases, following the
456 addition of O₃, HOBr (*m/z* 225 IHO⁸¹Br⁻), was observed together with Br₂ (Fig. 4, Fig. S4). We note in this case that
457 *m/z* 223, representative of IHO⁷⁹Br⁻, does not appear to show an enhancement when O₃ is added to the system. There
458 was a much higher background signal for *m/z* 223 compared with *m/z* 225 (IHO⁸¹Br⁻) resulting from an unknown
459 interference.

460 4 Summary and Conclusions

461 It was shown in this ice-coated wall flow tube laboratory study that the hydroxyl radical can act as an effective
462 condensed-phase halide oxidant leading to I₂, IBr, Br₂, and Cl₂ production under acidic conditions. Rates of molecular
463 halogen production and release were dictated by both pH and relative halide concentrations. The identities of the
464 molecular halogens produced appears to be highly influenced by which ions are enhanced at the ice surface, with I₂
465 production occurring prior to Br₂ production, which commenced as the [I⁻]/[Br⁻] was reduced. An opportunity exists
466 to further explore this chemistry via surface-sensitive methods, for which recent developments have been shown to
467 effectively enable characterization of the surface composition of frozen solutions of sodium chloride under near
468 atmospherically relevant conditions (Artiglia et al., 2017; Orlando et al., 2016). It would be useful to confirm the
469 dominant ions involved in this surface-based chemistry over time. Further investigations into the effects of halide
470 ratios on halogen production are also suggested, including measurements of how the ratios vary for different frozen
471 Arctic surfaces, as well as how they vary spatially. While condensed-phase OH produces Br₂ and I₂ most rapidly in

472 this study, it appears that other mechanisms, such as heterogeneous recycling of HOCl or ClONO₂, could be a more
473 dominant mechanism for in situ production of gas phase Cl₂ (Wang and Pratt, 2017). We find the addition of gas phase
474 O₃ produces additional Br₂ and I₂, likely through aqueous reactions with halides and/or gas-phase production of HOX
475 or possibly XONO₂ (Deiber et al., 2004) and subsequent halogen explosion chemistry. These results lend support for
476 the photochemical, condensed-phase molecular halogen production mechanisms proposed by the recent in situ
477 snowpack experiments (Custard et al., 2017; Pratt et al., 2013; Raso et al., 2017).

478 Understanding the environmental pH-dependence of halogen activation necessitates study of the pH on
479 relevant Arctic frozen surfaces. Pratt et al. (2013) found that the frozen surfaces most conducive to in-situ
480 photochemical Br₂ production had acidic pH after melting, while no production was observed from those with a well-
481 buffered alkaline ice brine. Similarly, we find herein that condensed-phase OH-induced halogen production is
482 enhanced at lower pH. Wren and Donaldson (2012a, 2012b) found in laboratory studies that pH of acidic and basic
483 solutions remains essentially unchanged after freezing, and that saline solutions with buffers (i.e., seawater) maintain
484 their buffering capacity following trace gas deposition, supporting the lack of observed Br₂ production from the sea
485 ice surface (Pratt et al., 2013). Therefore, it would be useful to test in-situ production of halogens from Arctic frozen
486 surfaces in tandem with measurement of the pH of said surfaces to determine the atmospherically relevant surface pH
487 range required for halogen production.

488
489 *Data availability.* Halfacre, J. W., Shepson, P. B., Pratt, K. A.: Laboratory experiments of the pH-dependent
490 production of molecular chlorine, bromine, and iodine from frozen saline surfaces, NSF Arctic Data Center,
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492
493 *Author contributions.* JWH and PBS designed the research and JWH performed the experiments and data
494 analysis. All three authors contributed to the discussion and interpretation of the results and writing of the paper.

495
496 *Competing interests.* The authors declare that they have no conflict of interest.

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669 **Tables**

670 Table 1: List of relevant species monitored by chemical ionization mass spectrometry ($\text{I}(\text{H}_2\text{O})_n^-$ as reagent ion) with corresponding
 671 m/z values.

Species	m/z
I^{81}Br^-	208
$\text{I}^{79}\text{Br}^{79}\text{Br}^-$	285
$\text{I}^{79}\text{Br}^{81}\text{Br}^-$	287
I^{35}Cl^-	162
I^{37}Cl^-	164
$\text{I}^{35}\text{Cl}^{35}\text{Cl}^-$	197
$\text{I}^{35}\text{Cl}^{37}\text{Cl}^-$	199
$\text{I}^{37}\text{Cl}^{37}\text{Cl}^-$	201
$\text{I}^{79}\text{Br}^{35}\text{Cl}^-$	241
$\text{I}^{81}\text{Br}^{35}\text{Cl}^- / \text{I}^{79}\text{Br}^{37}\text{Cl}^-$	243
I_3^-	381
IHO^{79}Br	223
IHO^{81}Br	225
$\text{IHO}_3^{5}\text{Cl}^-$	179
$\text{IHO}_3^{7}\text{Cl}^-$	181
IHOI^-	271
$\text{I}^{79}\text{IBr}^-$	333
$\text{I}^{81}\text{IBr}^-$	335

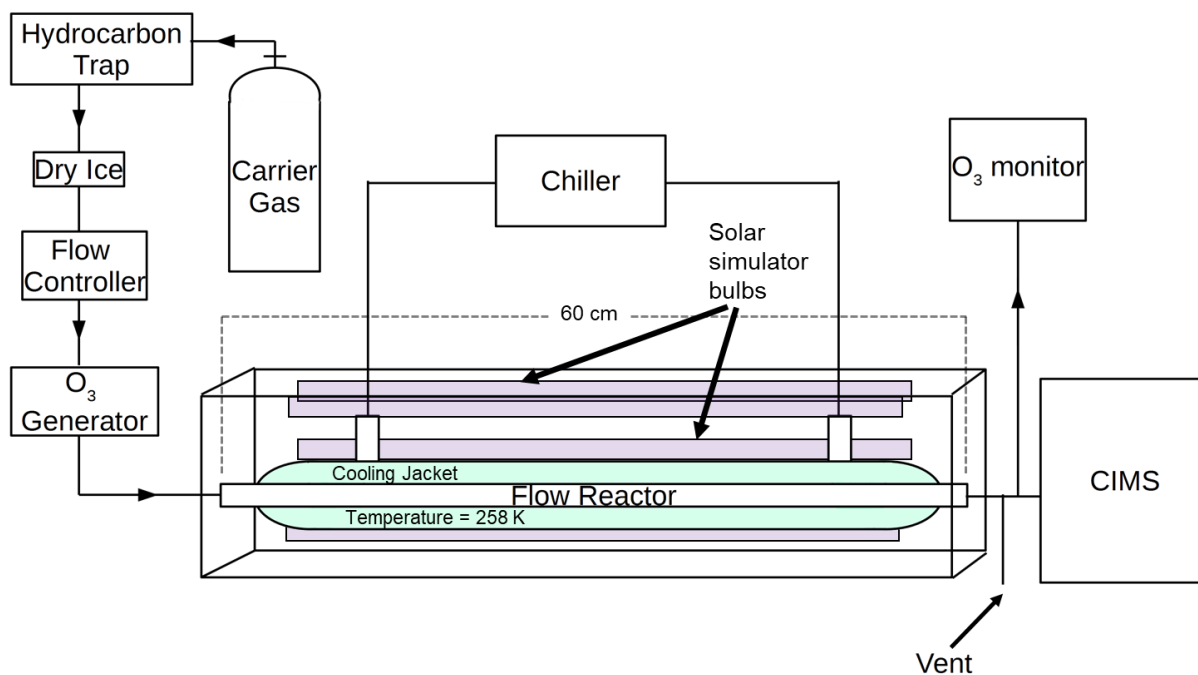
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674 Table 2: Results for all experiments performed. The first line in an experiment represents the integrated totals of molecular halogen
675 production after 1 hour of irradiation (t = 0 through t = 1 h). The results on italicized lines are 1 h integrated production amounts
676 beginning once additional ozone was introduced to the flow tube. Average LODs across experiments were 1.8 ± 0.4 , 1.2 ± 0.3 ,
677 and 9 ± 2 pmol mol⁻¹ for Br₂, Cl₂, and I₂ respectively. "IO#" represents samples composed of Instant Ocean, and "SW#" represents
678 "saltwater" samples, composed of reagent salts. "CL1" here represents the experiment performed using 0.557M high purity NaCl.
679 *The Br₂ and I₂ values presented for IO2 are discussed further in the Supplemental Information.

Experiment	Oxidant	pH	I ₂ produced (nmol)	Br ₂ produced (nmol)	Cl ₂ produced (nmol)
IO1	H ₂ O ₂ +O ₃	4.7	9 (±3) 22 (±8)	< LOD 0.06 (±0.05)	
IO2	H ₂ O ₂ +O ₃	4.7	*0.6 (±0.4) 21 (±14)	*0.034 (±0.003) 0.038 (±0.003)	
SW1	H ₂ O ₂ +O ₃	4.7	6.0 (±2.1) 51 (±19)	< LOD 0.024(±0.014)	
SW2	H ₂ O ₂ +O ₃	4.5	8 (±4) 51 (±25)	< LOD 0.018 (±0.003)	
IO3	NO ₂ ⁻	2.0	39 (±1)	0.084 (±0.002)	
IO4	H ₂ O ₂ +O ₃	1.7	0.8 (±0.3) < LOD	5.6 (±0.3) 12 (±1)	
IO5	H ₂ O ₂ +O ₃	1.7	0.33 (±0.11) 0.11 (±0.04)	3.5 (±0.4) 9.2 (±1.0)	
SW3	NO ₂ ⁻ +O ₃	1.8	4.0 (±0.1) < LOD	< LOD 0.46 (±0.1)	
SW4	NO ₂ ⁻ +O ₃	2.2	< LOD < LOD	5.4 (±0.7) 13 (±2)	
SW5	H ₂ O ₂ +O ₃	1.8	0.75 (±0.26) < LOD	6.0 (±0.7) 15 (±2)	
CL1	H ₂ O ₂	1.8	0.10 (±0.03)	0.10 (±0.01)	0.093 (±0.008)
IO6	None +O ₃	4.7	< LOD 26 (±9)	< LOD 0.015 (±0.001)	
IO7	None +O ₃	4.7	0.10 (±0.06) 47 (±29)	< LOD 0.012 (±0.001)	
SW6	None +O ₃	4.7	< LOD 80 (±1)	< LOD 0.16 (±0.01)	
SW7	None +O ₃	4.5	< LOD 48 (±2)	< LOD 0.023 (±0.001)	
IO8	None +O ₃	2.0	14 (±10) 2.6 (±1.7)	< LOD 0.14 (±0.02)	
SW8	None +O ₃	2.0	14 (±10) 2.6 (±1.7)	< LOD 0.14 (±0.02)	

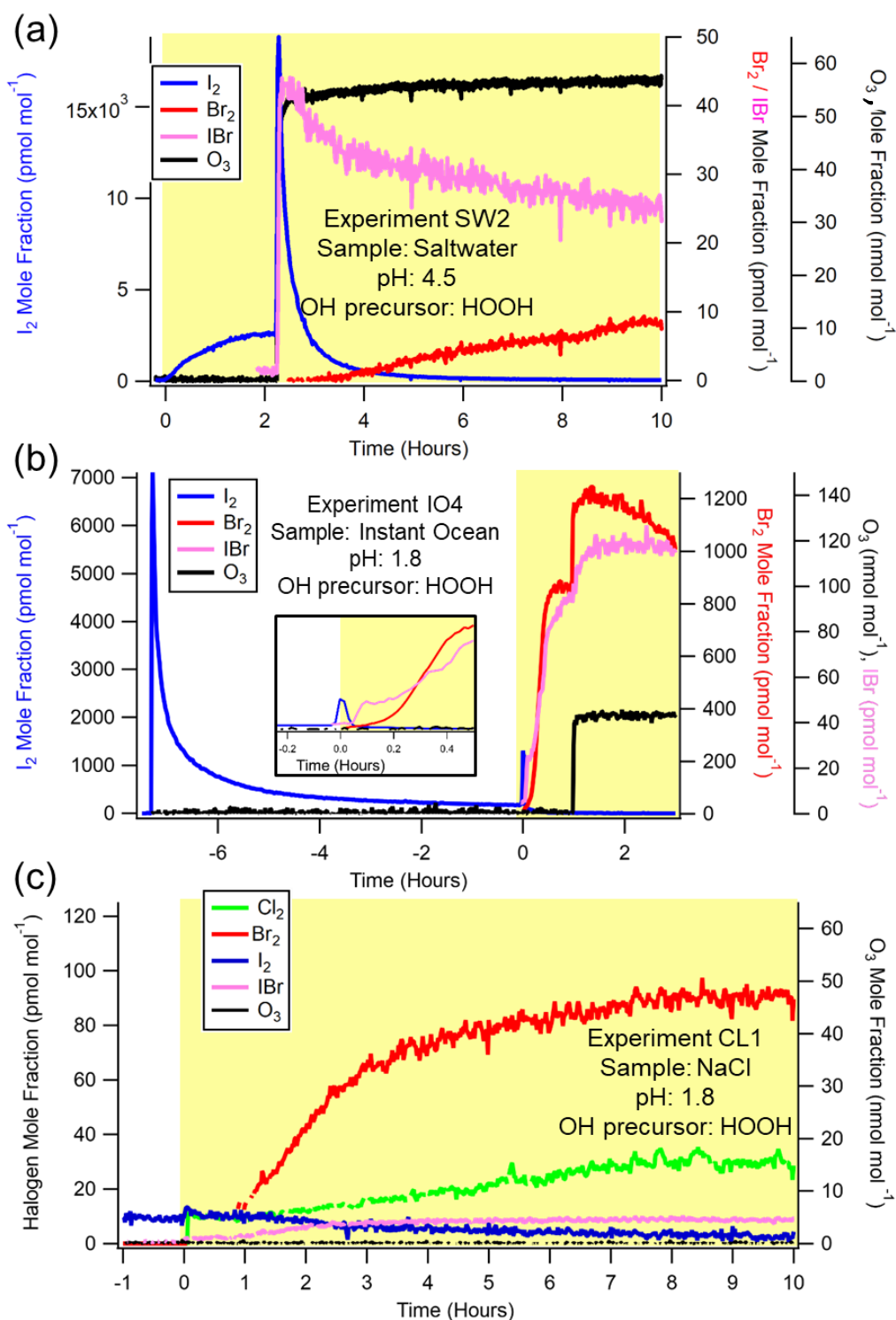
681 **Figures**



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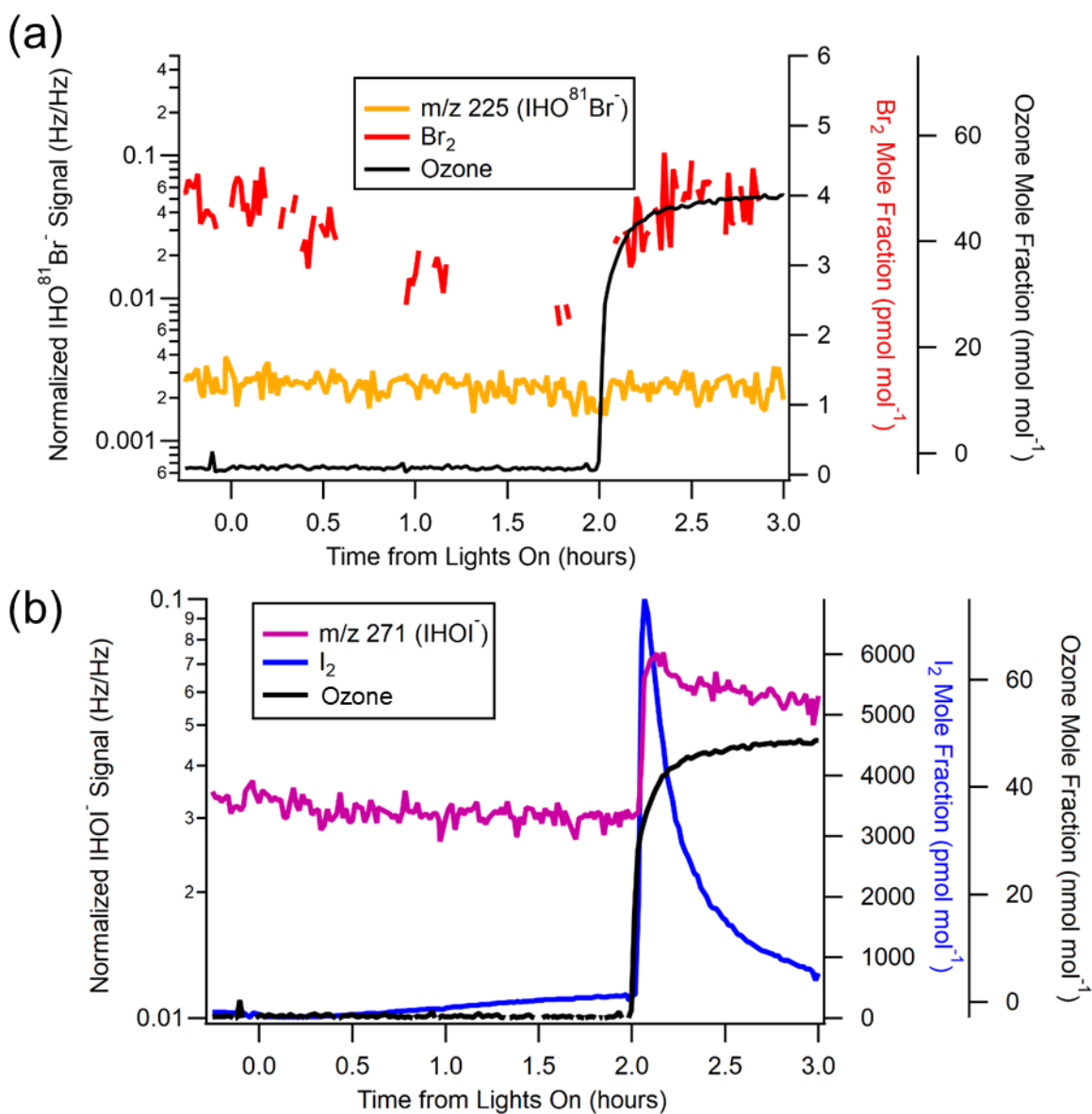
683 Figure 1: Experimental schematic. Purple bars represent powered solar simulator bulbs. The green shading around the flow tube
684 (flow reactor) represents cooling liquid (60% ethylene glycol, 40% water) circulated through the chiller. The flow reactor region
685 itself has an inner diameter of 2.5 cm.

686



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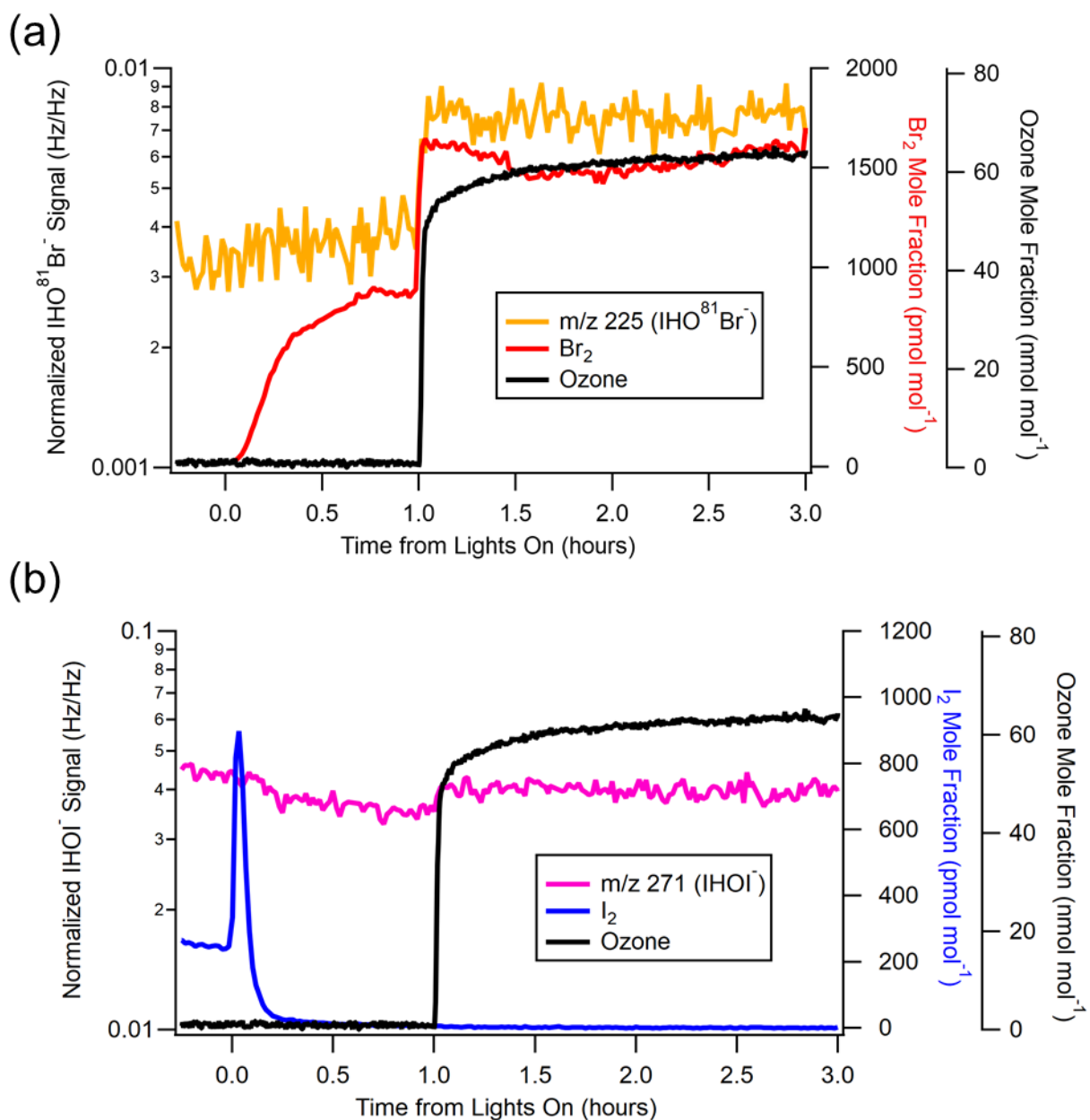
688 Figure 2: Representative experiments of OH-mediated production of X_2 , and subsequent production of X_2 from O_3 addition. a)
 689 Saltwater experiment (SW2) at pH=4.5. b) Instant Ocean experiment (IO4) at pH = 1.8. Time varying Br_2 and IBr signals before
 690 $t=0$ are shown in Fig. S2. Inset more clearly shows the increase of I_2 signal after irradiation. c) NaCl experiment (CL1) at pH = 1.8.
 691 Timescale represents hours from the activation of the lights, and the yellow shading represents presence of radiation from solar
 692 simulator bulbs. Gaps in data represent periods when the isotopic ratios showed an interference.



693

694 Figure 3: Normalized, background subtracted HOX signals from experiment IO2, pH=4.7. a) Comparison of Br_2 mole fractions to
 695 HOBr (m/z 225). Note that the HOBr signal should be considered only qualitatively as its identity could not be confirmed using
 696 isotopic ratios with m/z 223 due to its relatively large background signal. b) Effect of O_3 on I_2 and HOI.

697



698

699 Figure 4: Normalized, background subtracted HOX signals from experiment SW5, pH=1.8. a) Comparison of Br_2 mole fractions
 700 to HOBr (m/z 225). Note that the HOBr signal should be considered only qualitatively as its identity could not be confirmed using
 701 isotopic ratios with m/z 223. b) Effect of O_3 on I_2 and HOI.

702

1 2. Methods

2 2.1 Materials

3 Acetic acid/acetate and bisulfate/sulfate buffer concentrations were 20 mM (10 mM of each acid and
4 conjugate base). This concentration was chosen as a compromise between using as little buffer as possible and enough
5 buffer to ensure adequate buffering ability, as buffer capacity rapidly decreases as constituent species concentrations
6 approach the acid K_a value. The halide concentrations from our salt water solutions were Cl^- 500mM, Br^- 0.72mM,
7 and I^- 1.9×10^{-3} mM.

8 Given that the buffer concentration is comparable to or exceeds halide ion concentrations, there is a concern
9 that buffer composition may change over time due to the volatility of acetic acid (Henry's Law Constant of 400
10 M/atm), or because of buffer reactions with OH that may compete with reactions between OH and the halides:



15 Using these aqueous rate constants and the pre-freezing concentrations of species in our paper, we find the following
16 relative rates of OH-based production:

$$17 \frac{\frac{d[\text{X}_2]}{dt}}{\frac{d[\text{SO}_4^{\cdot-}]}{dt}} = 3.6 \times 10^5, 1.7 \times 10^3, 4.4 \text{ for } \text{Cl}_2, \text{Br}_2, \text{ and } \text{I}_2, \text{ respectively.}$$

$$18 \frac{\frac{d[\text{X}_2]}{dt}}{\frac{d[\text{CH}_3\text{CO}_2\text{H}]}{dt}} = 1.8 \times 10^4, 8.6 \times 10^1, 2.3 \times 10^{-1} \text{ for } \text{Cl}_2, \text{Br}_2, \text{ and } \text{I}_2, \text{ respectively.}$$

19 It is clear based on these relative rates of production that sulfate radical may contribute only a minor amount of Br^{\cdot}
20 and Cl^{\cdot} oxidation in our experiments, less than 0.1% of that from OH-halide oxidation.

21 No comparable rate constant could be found between I^- and sulfate. I_2 production may be impacted by
22 competition of the HSO_4^- and OH. Including dark production, however, I_2 was consistently our most abundant product
23 in all experiments except CL1 (in which only trace, undetectable iodide may have been present). Further, we do not
24 anticipate them occurring to an appreciable degree based on the fact that pH measurements before and after
25 experiments were identical (indicating no significant depletion of either buffer species throughout the experiment).

26

27 2.2 Flow tube

28 Reaction photochemistry was achieved using six UVA-340 solar simulator lamps (Q-Labs, 295 – 400 nm
29 with maximum wattage at 340 nm, irradiance spectrum in Fig. S1). These lamps were installed in the experiment box
30 (two on each side, except bottom). Each side was lined with reflective Mylar sheets to evenly irradiate the flow tube
31 when the lamps were powered.

32

33 2.3 CIMS

34 Experiments utilizing the bisulfate/sulfate buffer (IO3-5, IO8, SW3-5, SW8, and CL1) sometimes exhibited
35 cyclical CIMS signal changes for Br₂ (*m/z* 285, 287, 291), IBr (*m/z* 333, 335) with no attributable cause. These signal
36 changes occurred seemingly at random and to varying extents. In Fig. S2a, Experiment IO4 (pH = 1.7, includes H₂O₂)
37 demonstrates the most extreme example of this behaviour that almost appears to affect the analysis. First at t = -3, the
38 Br₂ rises briefly before falling. Then at t=2, the Br₂ signal begins to resemble a sine wave. All data beyond t=2 is not
39 considered for this specific experiment. In Fig S2b, the effect during Experiment SW5 (pH = 1.7, includes H₂O₂) is
40 more muted, beginning at approximately t = -6 for IBr and Br₂. As represented by these figures, this behaviour being
41 farther away from our periods of integration is typical of the remaining experiments. Because these signal changes
42 occurred outside of the experimental periods analyzed (i.e., before irradiation, and after O₃ had been active for one
43 hour), they are therefore not believed to affect our results and their interpretation.

44

45 3 Results and Discussion

46 3.1 Dark reaction production of I₂

47 In cases without OH precursors at pH < 2, significant photochemical I₂ production still occurs (integrated
48 production of 14 ± 10 nmol for IO8, and 6.0 ± 2.0 nmol for SW8), while Br₂ and Cl₂ concentrations remain below
49 limits of detection (consistent with Abbatt et al., (2010), in which no Br₂ was observed without an OH-precursor)
50 (Table 2, main text). This production likely stems from the mechanisms outlined by Kim et al. (2016) (R13-14, R10-
51 R12), discussed in the Sect. 1. As discussed in Sect. 3.1, H₂O₂ or NO₂⁻ can react directly with I⁻, thereby reducing the
52 available [I⁻] for photochemical OH oxidation when pH < 2. When H₂O₂ was the oxidant, integrated I₂ production

53 amounts were found to be ≤ 0.82 nmol (IO4, IO5, and SW5), likely due to this initial dark depletion. When instead
54 NO_2^- is used (as in IO3 and SW3), initial amounts of I_2 on flowtube connection to CIMS were less than when H_2O_2
55 was used (Table S1, Fig. S3). To estimate how much I⁻ may have been lost from our frozen sample by these dark
56 mechanisms, we convert the integrated I_2 production amounts from Table S1 to I⁻ (by multiplying by 2) and subtract
57 from the maximum possible moles of I⁻ in our samples ($0.0800 \text{ L} * 1.6 \times 10^{-6} \text{ M} = 1.28 \times 10^{-7}$ moles I⁻). For the
58 samples that use hydrogen peroxide, as little as 36–91% of I⁻ is available for reaction, while 94-97% remain when
59 using NO_2^- . However, it is certain that not all of the I_2 produced by this mechanism went into the CIMS by the nature
60 of having to break the flow tube seal in order to connect it to the CIMS. Therefore, these are only estimates that could
61 be affected by the length of time the tube is open to the environment and not connected to the CIMS, or sealed shut.

62

63 **3.2 Hydroxyl radical-induced halogen production**

64 **3.2.1 pH \approx 4.7**

65 Considering the values of I_2 production from Table 2 (main text), IO2, appears to have produced ~ 10 times
66 less I_2 based on the chosen period of integration. It was noted that I_2 appeared to already be present within the flow
67 tube on connecting the flow tube to the CIMS (Fig. S4). The integrated sum of I_2 released on connection of the flow
68 tube to the CIMS until stabilization was $0.8 (\pm 0.1)$ nmol, corresponding to approximately 0.5% of the total 152 nmol
69 I⁻ available for reaction from the Instant Ocean solution (Table S1). This production could possibly be induced by the
70 dark reactions described in Sect. 3.1. However, the experiment otherwise eventually produces the same qualitative
71 features as the other three experiments after light activation (Fig. S4). If instead the limits of integration are chosen
72 starting when the I_2 signal begins rising (i.e., during a period that qualitatively resembles the other experiments), the
73 integrated I_2 production amounts (1.1 ± 0.6 nmol) more closely approaches analogous experiments (IO1, SW1, SW2).
74 The apparent photochemical integrated Br_2 sum of 0.034 ± 0.003 nmol (Table 2) represents a real signal just above
75 the limit of detection (1.8 ± 0.4 pmol mol⁻¹), but this baseline signal does not change on addition of light (Fig. 3a). In
76 addition, the integration method used likely interpolated missing data for time periods in which incorrect isotope ratios
77 between m/z 285 and 287 were observed, thereby overestimating the integrated yield. This signal remains below
78 limits of quantitation and should not be considered further. Cl_2 concentrations remained below limits of detection for
79 experiment IO2.

80 In most cases, it was also found that extending limits of integration beyond 1 h after addition of O₃ did not
81 produce I₂ in amounts that exhausted the supply of I⁻. In an example experiment (IO2, Fig. S5), the limits of integration
82 were extended to t = 15 hours after the initiation of lights. While the signal appeared to stabilize below the I₂ LOD of
83 9 pmol mol⁻¹, the calculated I₂ production amount of 70 nmol for this extended integration period only accounts for
84 46% of the 152 total nmol of I⁻ available. When repeated for the other experiments at pH = 4.7, it is found that at least
85 16% of the original I⁻ remains unreacted after similarly extended limits of integration. This suggests that all of the I⁻
86 in our frozen samples may not be completely excluded to the disordered interface, and may exist within the ice bulk
87 or inaccessible brine channels throughout the ice, and that differences in integration production amounts can originate
88 from differences in I⁻ distribution during freezing (Bartels-Rausch et al., 2014; Malley et al., 2018).

89 **3.2.2 pH ≤ 2**

90 At low pH (~2), and with H₂O₂ as our OH precursor, we noted a large outflux of I₂ on connecting the flow
91 tube to the CIMS. Br₂ production was readily observed in the presence of light, and enhanced when the samples were
92 exposed to O₃, as in Fig 2b. However, experiment SW3 (Fig. S5), which was performed with NO₂⁻ as the hydroxyl
93 radical precursor, exhibited photochemical I₂ production on the introduction of radiation. Only after the introduction
94 of O₃ was Br₂ observed (under proper isotope ratios).

95

96 **3.3 Effects of O₃ on halogen production**

97 As discussed in the main text, HOX compounds were observed when O₃ was added to the flow tube. With
98 regard to the extent to which it affects our observed signal, we believe volatile organic compounds, such as aldehydes
99 and ketones, that may form gas phase HX could originate from our cylinder of zero air. However, we believe this
100 source would be effectively scrubbed by our activated charcoal trap (Fig. 1), mitigating any gas phase production of
101 HX. There also exists organic matter in the condensed phase, averaging 70 mg/L in each Instant Ocean sample (Sect.
102 2 of the main text). This carbon-matter is presumably uncharged and would freeze throughout the formed ice (i.e., no
103 freeze concentration effect), therefore making only a small fraction of the total carbon available at the frozen surface
104 for reaction.

105 If any of this solution-based carbon were involved in making HX, it would be expected that the SW and IO
106 experiments produce different amounts of IOHX⁻, given that the SW experiments were found to average ~5 mg/L of

107 dissolved organic matter. However, there is no difference in the signal changes between corresponding SW and IO
108 experiments (Figs. 3-4, S6). Therefore, we believe the primary source of IOHX⁻ in the CIMS is, indeed, HOX formed
109 in the flow tube.

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111

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139 **Tables**

140 Table S1: Integrated I₂ production amounts prior to irradiation or addition of O₃ from low pH experiments
141 involving samples with an OH precursor. The period of integration was chosen to be immediately after
142 connection of flow tube to the CIMS until sample was irradiated. Average LODs for I₂ across experiments
143 was 9 ± 2 pmol mol⁻¹. “IO#” represents samples composed of Instant Ocean, and “SW#” represents
144 “saltwater” samples, composed of reagent salts.

145

Experiment	Oxidant	pH	I ₂ produced (nmol)	Integration time (hours)	Estimated Percent of I ⁻ remaining for reaction
IO3	NO ₂ ⁻	2.0	4.0(±0.1)	0.55	93.7
SW4	NO ₂ ⁻	2.2	2.5(±0.1)	0.43	96.1
SW3	NO ₂ ⁻	1.8	2.0(±0.1)	0.83	96.8
IO4	H ₂ O ₂	1.7	41(±14)	7.28	36.2
IO5	H ₂ O ₂	1.7	5.7(±1.9)	2.92	91.1
SW5	H ₂ O ₂	1.8	41(±14)	4.95	35.5

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149 Table S2: Integrated I₂ produced from pH = 4.7 experiments involving samples with an OH precursor. The
150 period of integration begins at sample irradiation and extends past the limits of analysis used in the main
151 text. Average LODs for I₂ across experiments was 9 ± 2 pmol mol⁻¹. “IO#” represents samples composed
152 of Instant Ocean, and “SW#” represents “saltwater” samples, composed of reagent salts.

153

Experiment	Oxidant	pH	I ₂ produced (nmol)	Integration time (hours)	Estimated Percent of I ⁻ remaining for reaction
IO1	H ₂ O ₂	4.7	31(±10)	30	59
IO2	H ₂ O ₂	4.7	35(±20)	15	54
SW1	H ₂ O ₂	4.7	63(±23)	23	17
SW2	H ₂ O ₂	4.5	63(±20)	17	16

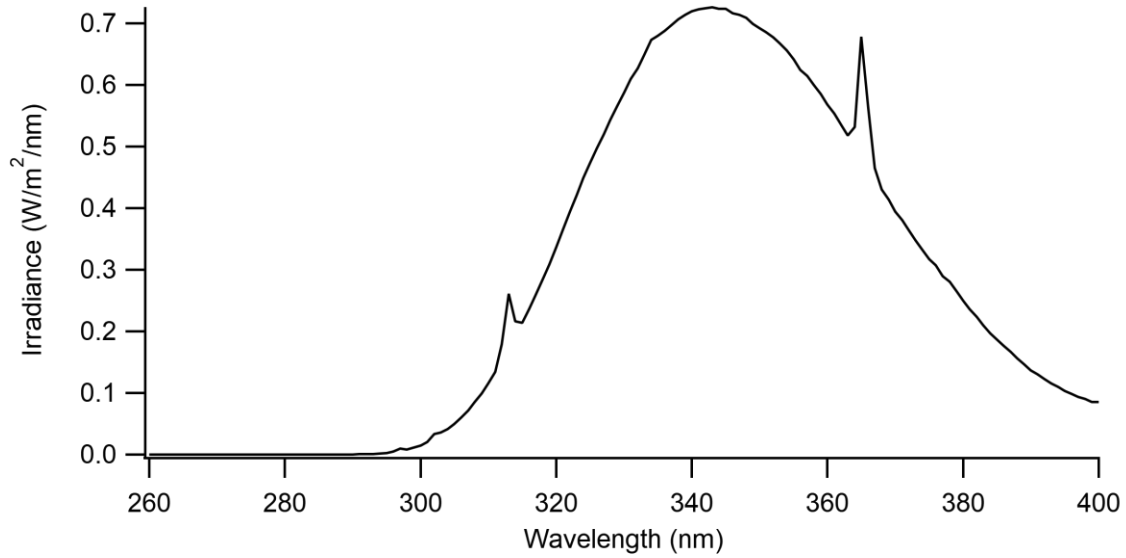
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158 **Figures**



159

160 Figure S1: Irradiance spectrum for the Q-Lab UVA 340 Lamps, reproduced with permission from Q-Lab
161 Corporation Technical Bulletin LU-8052 – “SPD for QUV UVA-340.”

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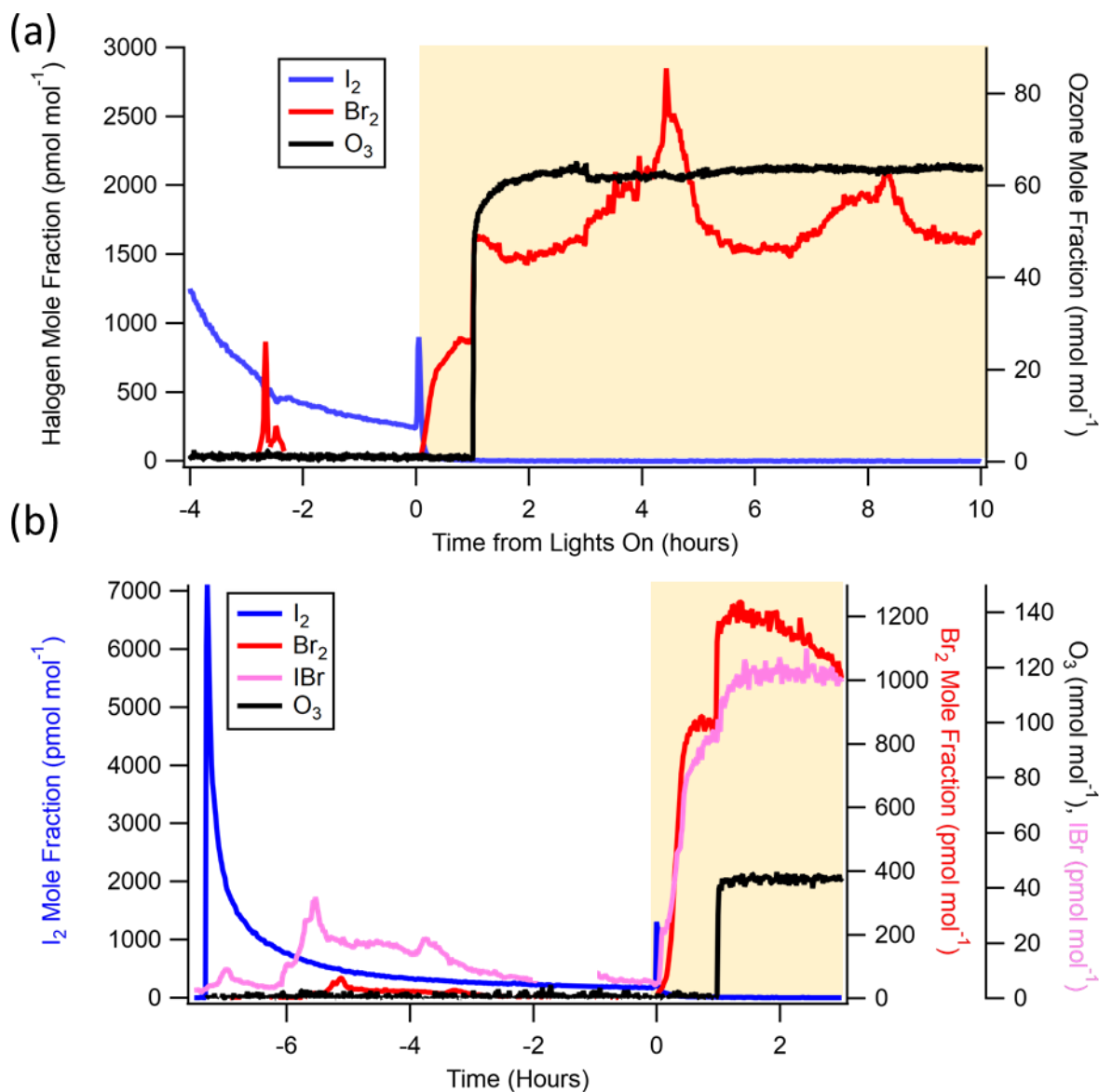
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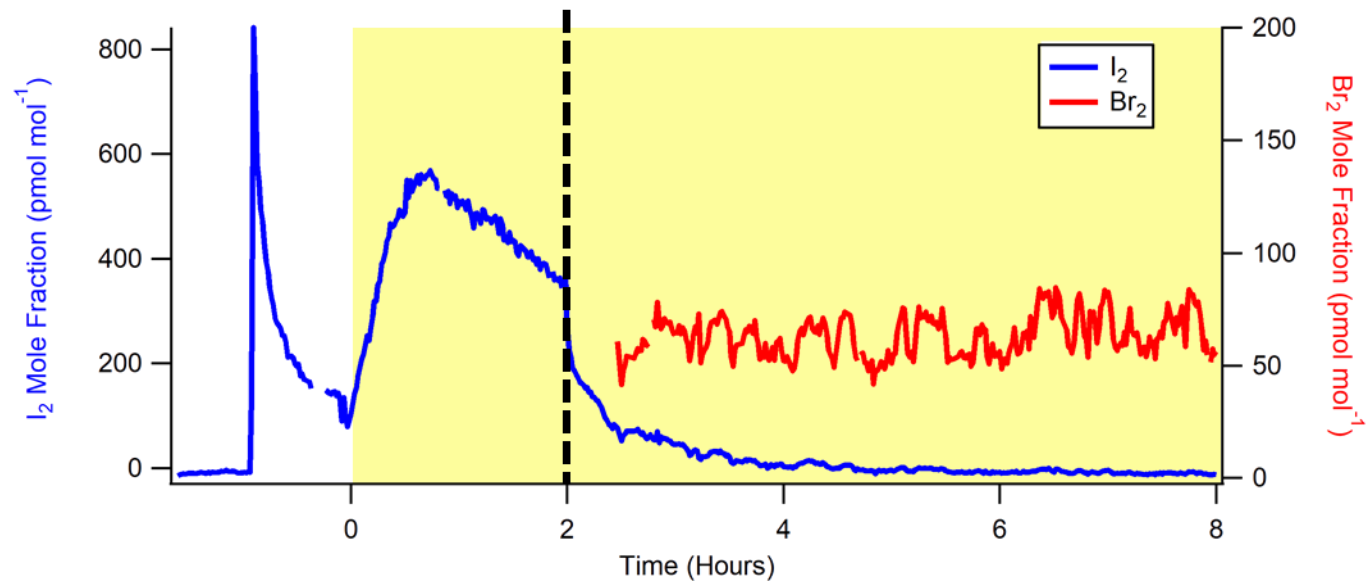
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 179 Figure S2: a) Experiment IO4 (pH < 2, includes H₂O₂) time series demonstrating cyclical increases in signal
 180 Br₂ signals, especially at t= -3 and beginning again at t = 2. Period of analysis in main text includes t = 0
 181 until t=2. b) Experiment SW5 (pH < 2, includes H₂O₂) time series demonstrating cyclical signals for IBr
 182 and Br₂, beginning predominately at t = -6 until shortly before t = 0.

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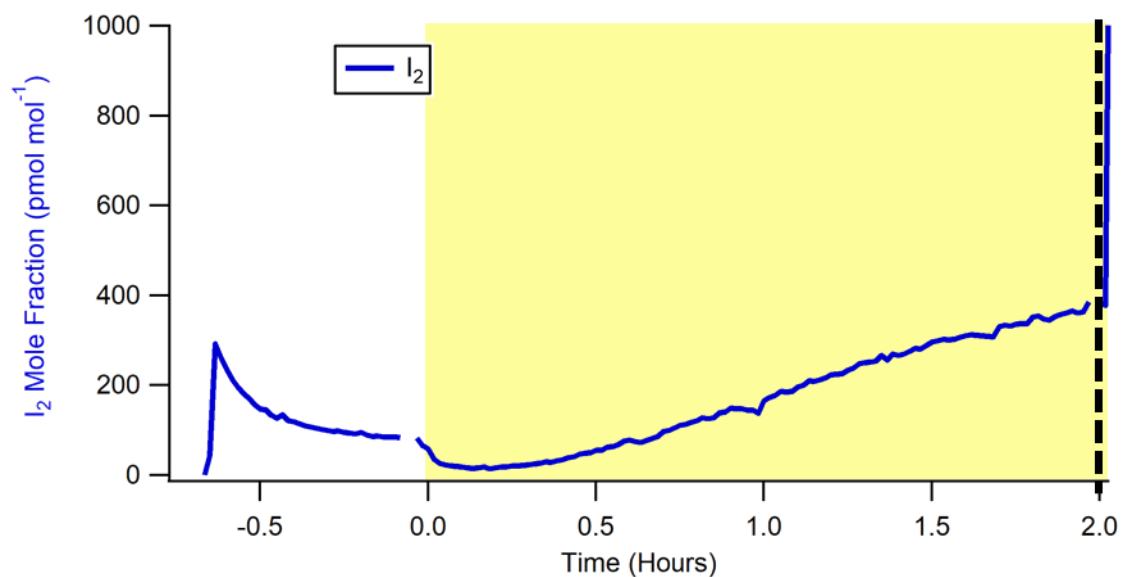


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189 Figure S3: Experiment SW3, using synthetic seawater at pH = 1.8, in which NO₂⁻ acted as our hydroxyl
 190 radical precursor. Ozone was introduced at hour two (indicated by dashed vertical line), coincident with
 191 the I₂ concentration decrease. Br₂ data filtered based on correctness of isotope ratios between *m/z* 285 and
 192 287 (IBrBr).

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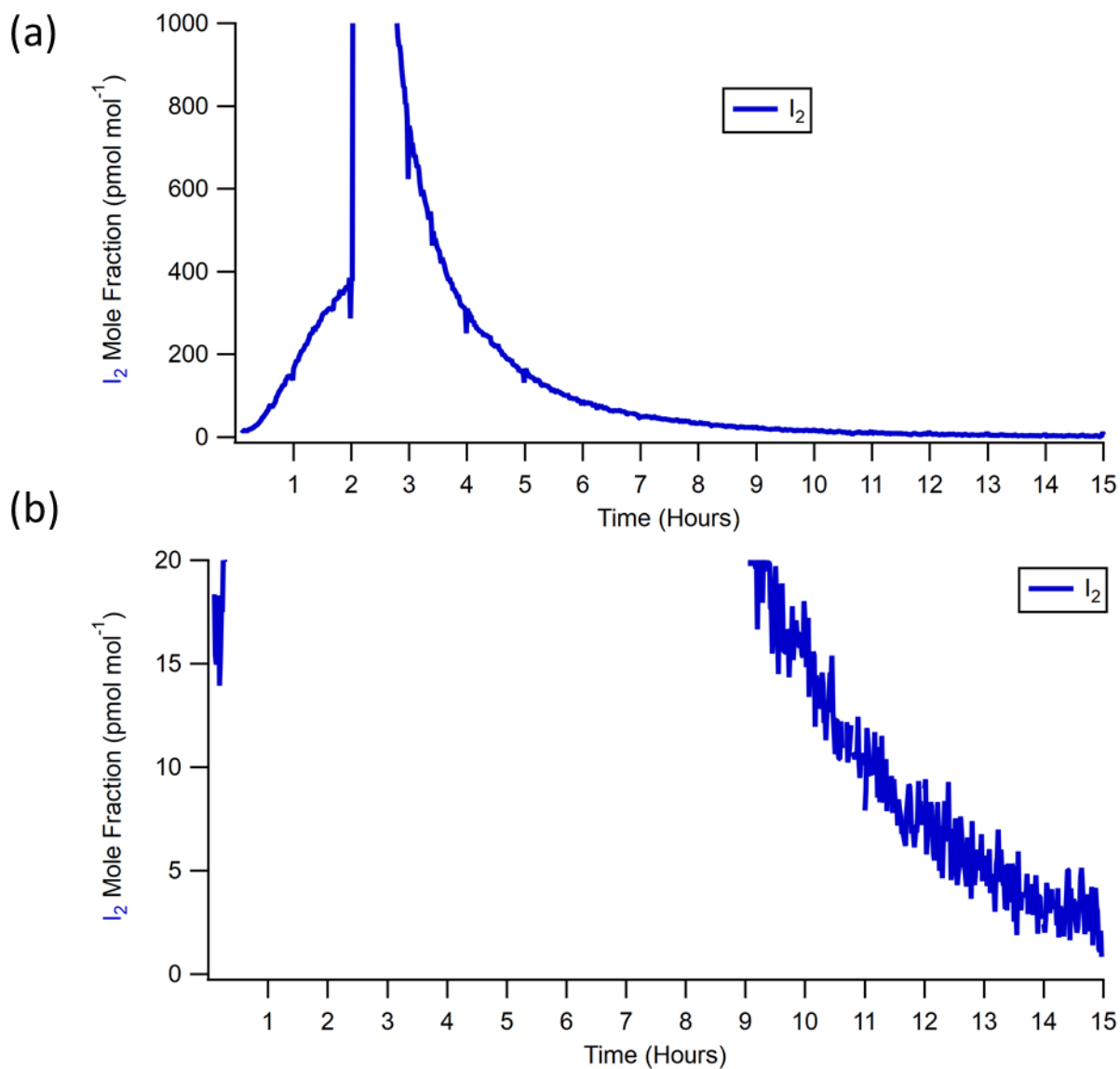


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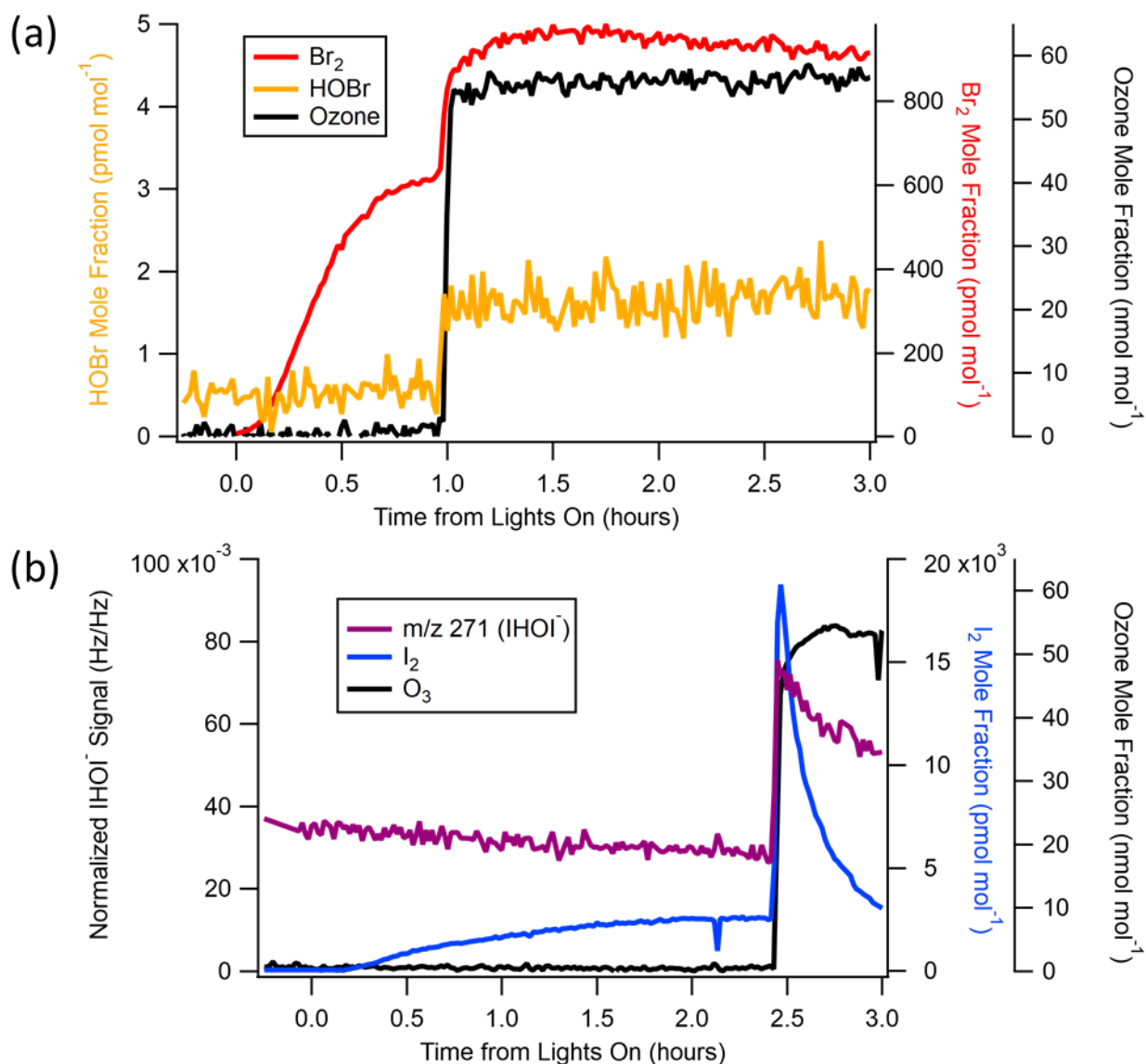
197 Figure S4: Experimental timeseries for experiment IO2. The key difference between this experiment and
198 others at pH ~4.68 is that there was some initial I₂ present when the flow tube was connected to the CIMS.
199 On activating the lights, these concentrations lowered, before ultimately rising due to OH-induced I₂
200 production. Beginning the integration when the signal begins rising leads to similar production values as
201 those experiments without this initial I₂ present. Vertical dashed line represents when O₃ was introduced
202 to the system.

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Figure S5: Iodine time series from experiment IO2, using Instant Ocean at pH = 4.7, in which H₂O₂ acted as our hydroxyl radical precursor. The x-axis begins on light introduction to the flow tube, while ozone was introduced at hour two as indicated by the sudden increase in signal. (a) The time series signal rapidly increases at t=2 coincident with the addition of 60 nmol mol⁻¹ of O₃, and then returns to baseline by hour 13. (b) Zoomed in version of the same plot



213

214 Figure S6: a) Experiment IO5, using Instant Ocean at pH = 1.7, in which H_2O_2 acted as our hydroxyl radical
 215 precursor (analogous to SW5, Fig. 4). Comparison of Br_2 mole fractions to HOBr. Note that the HOBr
 216 signal should be used only for qualitative purposes as its identity could not be confirmed using isotopic
 217 ratios with m/z 223 due to its relatively large background signal. Br_2 data filtered based on correctness of
 218 isotope ratios between m/z 285 and 287 (IBrBr^-). b) Experiment SW2 (analogous to IO2, Fig. 3) showing
 219 effect of O_3 on I_2 and HOI.

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221